IV.1 $\boxed{H_D = \frac{\gamma_1\gamma_2}{r^3}\left[\overline{I}_1\cdot\overline{I}_2 - \frac{3(\overline{I}_1\cdot\overline{r})(\overline{I}_2\cdot\overline{r})}{r^2}\right]}$ m+1

All here is just problem I

$I_1 = (I_{1x}, I_{1y}, I_{1z}) \quad I_2 = (I_{2x}, I_{2y}, I_{2z})$

$\overline{I}_1\cdot\overline{I}_2 = I_{1x}I_{2x} + I_{1y}I_{2y} + I_{1z}I_{2z}$

$I_x = \frac{I_+ + I_-}{2} \qquad I_y = \frac{I_+ - I_-}{2i}$

$\overline{I}_1\cdot\overline{I}_2 = \left(\frac{I_{1+}+I_{1-}}{2}\right)\left(\frac{I_{2+}+I_{2-}}{2}\right) + \left(\frac{I_{1+}-I_{1-}}{2i}\right)\left(\frac{I_{2+}-I_{2-}}{2i}\right) + I_{1z}I_{2z}$

$= \frac{1}{4}\left[\cancel{I_{1+}I_{2+}} + I_{1+}I_{2-} + I_{1-}I_{2+} + \cancel{I_{1-}I_{2-}}\right]\left(\frac{1}{4}\right)$

$+ \left[-\cancel{I_{1+}I_{2+}} + I_{1+}I_{2-} + I_{1-}I_{2+} - \cancel{I_{1-}I_{2-}}\right]\left(1/4\right)$

$= \frac{2 I_{1+}I_{2-} + I_{1-}I_{2+}}{4} + I_{1z}I_{2z} \Rightarrow \boxed{\overline{I}_1\overline{I}_2 = \frac{I_{1+}I_{2-} + I_{1-}I_{2+}}{2} + I_{1z}I_{2z}}$

$\overline{r}_{12} = (r\,s(\theta)c(\phi),\ r\,s(\theta)s\phi,\ r\,c(\theta))$

$\overline{I}_1\cdot\overline{r}_{12} = I_{1x}\,r\,s\theta c\phi + I_{1y}\,r\,s\theta s\phi + I_{1z}\,r\,c\theta$

$\overline{I}_2\cdot\overline{r}_{12} = I_{2x}\,r\,s\theta c\phi + I_{2y}\,r\,s\phi s\phi + I_{2z}\,r\,c\theta$

$\frac{(\overline{I}_1\cdot\overline{r}_{12})(\overline{I}_2\cdot\overline{r}_{12})}{r^2} = I_{1x}\,r\,s\theta c\phi\left[I_{2x}\,r\,s\theta c\phi + I_{2y}\,r\,s\theta s\phi + I_{2z}\,r\,c\theta\right]$

$+ I_{1y}\,r\,s\theta s\phi\left[\quad\right] + I_{1z}\left(\quad\right]$

r^2 Drops out

MZ1

$I_1 \cdot I_2$

$r = (r s\theta c\phi, r s\theta s\phi, r c\theta)$

$\bar{I}_1 \cdot \bar{r} = I_{1x} r s\theta c\phi + I_{1y} r s\theta s\phi + I_{1z} r c\theta$

$\bar{I}_2 \bar{r} = I_{2x} r s\theta c\phi + I_{2y} r \theta s\theta + I_{2z} r c\theta)$

$$\frac{(\bar{I}_1 \cdot \bar{r})(\bar{I}_2 \cdot \bar{r})}{r^2} = s^2\theta c^2\phi (I_{1x} I_{2x})$$
$$+ s^2\theta s^2\phi (I_{1y} I_{2y})$$
$$+ c^2\theta (I_{1z} I_{2z})$$
$$+ s^2\theta c\phi s\phi (I_{1x} I_{2y})$$
$$+ s^2\theta s\phi c\phi (I_{2x} I_{1y})$$
$$+ s\theta c\theta c\phi (I_{1x} I_{2z})$$
$$+ s\theta c\theta c\phi (I_{2x} I_{1z})$$
$$+ s\theta c\theta s\phi (I_{1y} I_{2z})$$
$$+ s\theta c\theta s\phi (I_{2y} I_{1z})$$

OC

MZ 2

$$= s^2\theta c^2\phi\left[\frac{(I_{1+}+I_{1-})(I_{2+}+I_{2-})}{4}\right]$$

break down together

$$+ s^2\theta s^2\phi\left[\left(\frac{I_{1+}-I_{1-}}{2i}\right)\left(\frac{I_{2+}-I_{2-}}{2i}\right)\right]$$

$$+ c^2\theta\left[I_{1z}I_{2z}\right]$$

$$+ s^2\theta c\phi s\phi\left[\left(\frac{I_{1+}+I_{1-}}{2}\right)\left(\frac{I_{2+}-I_{2-}}{2i}\right)+\left(\frac{I_{2+}+I_{2-}}{2}\right)\left(\frac{I_{1+}-I_{1-}}{2i}\right)\right]$$

$$+ s\theta c\theta c\phi\left[\left(\frac{I_{1+}+I_{1-}}{2}\right)I_{2z}+\left(\frac{I_{2+}+I_{2-}}{2}\right)I_{1z}\right]$$

together

$$+ s\theta c\theta s\phi\left[\left(\frac{I_{1+}-I_{1-}}{2i}\right)I_{2z}+\left(\frac{I_{2+}-I_{2-}}{2i}\right)I_{1z}\right]$$

OK

$c^2t - s^2t = c(2t)$

$s(2t) = 2s(t)c(t)$

$$= \cancel{I_4}\; s^2\theta(c^2\phi - s^2\phi)\left[I_{1+}I_{2+}\right]$$

$$+ s^2\theta(c^2\phi - s^2\phi)\left[I_{1-}I_{2-}\right]$$

$$+ \frac{s^2\theta}{4}\left[I_{1+}I_{2-}+I_{1-}I_{2+}\right]$$

$$+ c^2\theta\left[I_{1z}I_{2z}\right] \checkmark$$

$$+ s^2\theta s\phi c\phi\left[\frac{2I_{1+}I_{2+}-2I_{1-}I_{2-}}{4i}\right] \checkmark$$

$$+ s\theta c\theta\left[I_{1+}I_{2z}e^{-i\phi}+I_{1-}I_{2z}e^{i\phi}+I_{2+}I_{1z}e^{-i\phi}+I_{2-}I_{1z}e^{i\phi}\right]$$

$$= s^2\theta\, c(2\phi)\left[\frac{I_{1+}I_{2+} + I_{1-}I_{2-}}{4}\right) \checkmark$$

MZ3

$$+ s^2(\theta)\left[\frac{I_{1+}I_{2-} + I_{1-}I_{2+}}{4}\right) \checkmark$$

$$+ c^2\theta\left(I_{1z}I_{2z}\right) \checkmark$$

$$+ s^2\theta\, s(2\phi)\left[\frac{I_{1+}I_{2+} - I_{1-}I_{2-}}{4i}\right] \checkmark$$

$$+ s\theta c\theta\left[I_{1+}I_{2z}e^{-i\phi}\, I_{1-}I_{2z}e^{-i\phi} + I_{2+}I_{1z}e^{-i\phi} + I_{2-}I_{1z}e^{i\phi}\right]$$

~~3~~ MZ4

$$\frac{I_1 \cdot I_2 - 3(I_1 \cdot r)(I_2 \cdot r)}{r^2} =$$

$$\frac{I_{1+} I_{2-} + I_{1-} I_{2+}}{2} + I_{1z} I_{2z}$$

$$- s^2\theta\, c2\phi \left[\frac{3}{4} \left(I_{1+} I_{2+} + I_{1-} I_{2-} \right) \right]$$

$$- s^2(\theta) \left[\frac{3}{4} \left(I_{1+} I_{2-} + I_{1-} I_{2+} \right) \right]$$

$$- c^2\theta \left[-3 I_{1z} I_{2z} \right]$$

$$- s^2\theta\, c^2\phi \left[\left(\frac{3}{4i} \right) \left(I_{1+} I_{2+} - I_{1-} I_{2-} \right) \right]$$

$$- s\theta\, c\phi \left[\left(\frac{3}{2} \right) \left(I_{1+} I_{2z} e^{-i\phi} + I_{1-} I_{2z} e^{i\phi} + I_{2+} I_{1z} e^{-i\phi} + I_{2-} I_{1z} e^{i\phi} \right) \right]$$

$$= \frac{(3c^2\theta - 1)}{4} \left[I_{1+} I_{2-} - I_{1-} I_{2+} \right]$$

Sign is wrong
see my derivation

$$- (3c^2\theta - 1)\left(I_{1z} I_{2z} \right]$$

$$- s^2\theta \left[\left(\frac{3}{4} \right) \left(I_{1+} I_{2+} e^{i2\phi} \right) \right]$$

$$- s^2\theta \left[\left(\frac{3}{4} \right) I_{1-} I_{2-} e^{-i2\phi} \right) \right]$$

$$- s\theta c\phi e^{-i\phi} \left[I_{1+} I_{2z} + I_{2+} I_{1z} \right) \left(\frac{3}{2} \right) \checkmark$$

$$- s\theta c\phi\, e^{i\phi} \left[I_{1-} I_{2z} + I_{1z} I_{2-} \right) \left(\frac{3}{2} \right) \checkmark$$

$(I_{1+} I_{2+} + I_{1-} I_{2+} + I_{1+} I_{2-} + I_{1-} I_{2-}) s^2\theta c^2\phi$

$- (I_{1+} I_{2+} - I_{1-} I_{2+} - I_{1+} I_{2-} + I_{1-} I_{2-}) s^2\theta s^2\phi$

$A s^2\theta c^2\phi - B s^2\theta s^2\phi$

$A s^2\theta (1 - s^2\phi) - B s^2\theta s^2\phi$

$A s^2\theta - A s^2\theta s^2\phi - B s^2\theta s^2\phi$

$A s^2\theta - s^2\theta s^2\phi [A - B]$

$A s^2\theta - s^2\theta s^2\phi$

$A \cancel{s^2\theta - s^2\theta s^2\phi C}$

$I_x = \frac{I_+ + I_-}{2}$

$I_y = \frac{I_+ - I_-}{2i}$

---

start here $s^2\theta c^2\phi (A) + s^2\theta s^2\phi (B)$

$s^2\theta (A c^2\phi + B s^2\phi)$

$s^2\theta \left[(I_{1x} I_{2x}) c^2\phi + (I_{1y} I_{2y}) s^2\phi \right]$

$s^2\theta \left[\frac{(I_{1+} + I_{1-})(I_{2+} + I_{2-})}{4} c^2\phi - \frac{(I_{1+} - I_{1-})(I_{2+} - I_{2-})}{4} s^2\phi \right]$

$\frac{s^2\theta}{4} \left[(I_{1+} I_{2+} + I_{1+} I_{2-} + I_{1-} I_{2+} + I_{1-} I_{2-}) c^2\phi - (I_{1+} I_{2+} - I_{1+} I_{2-} - I_{1-} I_{2+} + I_{1-} I_{2-}) \frac{s^2\phi}{4} \right]$

$$\cancel{c^2\phi}\ \frac{s^2\theta}{4}\left\{\begin{array}{l} c^2\phi\, I_{1+}I_{2+} - s^2\phi\, I_{1+}I_{2+} \\ c^2\phi\, I_{1+}I_{2-} + s^2\phi\, I_{1+}I_{2-} \\ c^2\phi\, I_{1-}I_{2+} + s^2\phi\, I_{1-}I_{2+} \\ c^2\phi\, I_{1-}I_{2-} - s^2\phi\, I_{1-}I_{2-} \end{array}\right)$$

$$\boxed{\begin{array}{l} c^2\phi - s^2\phi = c(2\phi) \\ c^2 + s^2 = 1 \end{array}}$$

use

$$\boxed{s(2t) = 2s(t)c(t)}$$

$$= \frac{s^2\theta}{4}\begin{array}{l} I_{1+}I_{2+}(c^2 - s^2) \\ + I_{1+}I_{2-}(c^2 + s^2) \\ + I_{1-}I_{2+}(c^2 + s^2) \\ + I_{1-}I_{2-}(c^2 - s^2) \end{array}$$

$$= \begin{array}{l} I_{1+}I_{2+}\, c(2\phi) \\ + I_{1+}I_{2-} \\ + I_{1-}I_{2+} \\ + I_{1-}I_{2-}\, c(2\phi) \end{array}$$

$$= s^2\theta\, c(2\phi)\left(I_{1+}I_{2+} + I_{1-}I_{2-}\right)$$

$$+ s^2\theta\left(I_{1+}I_{2-} + I_{1-}I_{2+}\right)$$

✓ Yes!

$$\frac{s^2\theta\, c\phi\, s\phi}{4i}\Big[I_{1+}I_{2+} - I_{1-}I_{2-} + I_{1-}I_{2+} - I_{1-}I_{2-} + I_{1+}I_{2+} + I_{1+}I_{2-} - I_{1-}I_{2+} - I_{1-}I_{2-} \Big]$$

$$I_x = \frac{I_+ + I_-}{2}$$

$$I_y = \frac{I_+ - I_-}{2i}$$

$$s^2\theta\, c\phi\, s\phi \left[I_{1x} I_{2y} + I_{1y} I_{2x} \right]$$

$$= \left(\frac{I_{1+} + I_{1-}}{2}\right)\left(\frac{I_{2+} - I_{2-}}{2i}\right) + \left(\frac{I_{1+} - I_{1-}}{2i}\right)\left(\frac{I_{2+} + I_{2-}}{2}\right)$$

$$\left(\frac{1}{4i}\right)\Big[I_{1+}I_{2+} - \cancel{I_{1+}I_{2-}} + \cancel{I_{1-}I_{2+}} - I_{1-}I_{2-} + I_{1+}I_{2+} + \cancel{I_{1+}I_{2-}} - \cancel{I_{1-}I_{2+}} - I_{1-}I_{2-} \Big]$$

$$= \frac{1}{4i}\Big[2 I_{1+} I_{2+} - 2 I_{1-} I_{2-} \Big] = \frac{1}{2i}\Big[I_{1+}I_{2+} - I_{1-}I_{2-} \Big] s^2\theta\, c\phi\, s\phi$$

$$\frac{2 s^2\theta\, c\phi\, s\phi}{4i}\Big[I_{1+}I_{2+} - I_{1-}I_{2-} \Big]$$

$$\boxed{2c(t)s(t) = s(2t)}$$

use

$$\frac{s^2\theta\, s(2\phi)}{4i}\Big[I_{1+}I_{2+} - I_{1-}I_{2-} \Big]$$

✓

$s\theta c\theta c\phi\,[A] + s\theta c\theta s\phi\,[B]$

$c + is = e^{i\phi}$

$c - is = e^{-i\phi}$

Write out all terms then separate by spin parts ⋮ gives

$$s\theta c\theta c\phi \left[\frac{I_{1+}I_{2z} + I_{1-}I_{2z} + I_{1z}I_{2+} + I_{1z}I_{2-}}{\cancel{4}\ 2} \right]$$

$$+ s\theta c\theta s\phi \left[\frac{I_{1+}I_{2z} - I_{1-}I_{2z} + I_{1z}I_{2+} - I_{1z}I_{2-}}{\cancel{4}i} \right]$$

$$= \frac{2 I_{1z}I_{2z}\, s\theta c\theta}{4} \left[c\phi + \frac{s\phi}{i} \right] \Rightarrow \boxed{\frac{I_{1z}I_{2z}\, s\theta c\theta}{2} e^{-i\phi}}$$

$$s\theta c\theta c\phi \frac{I_{1-}I_{2z}}{4} - \frac{s\theta c\theta s\phi\, I_{1-}I_{2z}}{4i}$$

$$\cancel{= s\theta c\theta\, I_{1z}}$$

$$= \frac{I_{1-}I_{2z}\, s\theta c\theta}{4} \left[c\phi - \frac{s\phi}{i} \right]$$

$$= \boxed{\frac{I_{1-}I_{2z}\, s\theta c\theta}{\cancel{4}\,2} e^{i\phi}}$$

$$\frac{s\theta c\theta}{2} I_{1z} I_{2+} \left[c\phi + \frac{s\phi}{i} \right] =$$

$$= \boxed{\frac{s\theta c\theta}{2} I_{1z} I_{2+} e^{-i\phi}}$$

$$\frac{s\theta c\theta}{2} I_{1z} I_{2-} \left[c\phi - \frac{s\phi}{i} \right] = \frac{s\theta c\theta}{2} I_{1z} I_{2-} e^{i\phi}$$

All

$$\frac{s\theta c\theta}{2} \left[I_{1+} I_{2z} e^{-i\phi} + I_{1-} I_{2z} e^{i\phi} + I_{1z} I_{2+} e^{-i\phi} + I_{1z} I_{2-} e^{i\phi} \right]$$

$$\boxed{\begin{aligned} &\frac{s\theta c\theta}{2} e^{-i\phi} \left[I_{1+} I_{2z} + I_{1z} I_{2+} \right] \\ &\frac{s\theta c\theta}{2} e^{i\phi} \left[I_{1-} I_{2z} + I_{1z} I_{2-} \right] \end{aligned}}$$

$=$

$$I_{1z}I_{2z} - 3c^2\theta(I_{1z}I_{2z})$$

$$+\left(\frac{I_{1+}I_{2-} + I_{1-}I_{2+}}{2}\right) - \frac{3}{4}s^2\theta[I_{1+}I_{2-} + I_{1-}I_{2+}]$$

$$-\frac{3}{4}s^2\theta c(2\phi)[A] - \frac{3}{4i}s^2\theta s(2\phi)[A]$$

$$+C + D$$

$$= I_{1z}I_{2z}(1-3c^2\theta) \quad \text{Done} \ (A)$$

$$-\frac{3}{4}s^2\theta[A]\left(c(2\phi - \frac{s(2\phi)}{i})\right)$$

$$+ \ldots$$

$$= I_{1z}I_{2z}(1-3c^2\theta)$$

$$-\frac{3}{4}s^2\theta[I_{1+}I_{2+} + I_{1-}I_{2-}]e^{2i\phi}$$

WORK ON $s^2\theta$ & $I_{1+}I_{2-}$ ... terms

$$\frac{I_{1+}I_{2-} + I_{1-}I_{2+}}{2} - \frac{3}{4} s^2\theta \left[I_{1+}I_{2-} + I_{1-}I_{2+} \right]$$

$$A - \frac{3}{2} s^2\theta [A]$$

$$A - \frac{3}{2}(1 - c^2\theta) A$$

$$A - \frac{3}{2} A - c^2\theta A$$

$$-\frac{A}{2} - c^2\theta A$$

$$+\frac{A}{2}\left(-\frac{1}{2} - c^2\theta\right)$$

$$\frac{A}{2} - \frac{3}{4} s^2\theta [A]$$

$$A\left[\frac{1}{2} - \frac{3}{4} s^2\theta\right]$$

$$A\left[\frac{1}{2} - \frac{3}{4}(1 - c^2\theta)\right]$$

$$A\left[\frac{1}{2} - \frac{3}{4} + \frac{3}{4} c^2\theta\right]$$

$$A\left[-\frac{1}{4} + \frac{3}{4} c^2\theta\right]$$

$$-\frac{A}{4}\left[1 - 3c^2\theta\right] = \boxed{-\frac{\left[I_{1+}I_{2-} + I_{1-}I_{2+}\right]}{4}\left[1 - 3c^2\theta\right]}$$

Done (B)

$$\frac{(\bar{I}_1\cdot\bar{r})(\bar{I}_2\cdot\bar{r})}{r^2} \Rightarrow$$

$$+ c^2(\theta)(I_{1z}I_{2z})$$

$$+ s^2\theta\, c(2\phi)\left[\frac{I_{1+}I_{2+} + I_{1-}I_{2-}}{4}\right]$$

$$+ s^2\theta\left[\frac{I_{1+}I_{2-} + I_{1-}I_{2+}}{4}\right]$$

$$+ \frac{s^2\theta\, s(2\phi)}{4i}\left[I_{1+}I_{2+} - I_{1-}I_{2-}\right]$$

$$+ \frac{\cos\theta}{2} e^{-i\phi}\left[I_{1+}I_{2z} + I_{1z}I_{2+}\right]$$

$$+ \frac{\cos\theta}{2} e^{i\phi}\left[I_{1-}I_{2z} + I_{1z}I_{2-}\right]$$

$$\bar{I}_1\cdot\bar{I}_2 - 3\frac{(\bar{I}_1\cdot\bar{r})(\bar{I}_2\cdot\bar{r})}{r^2} \Rightarrow$$

$$-3c^2\theta\,(I_{1z}I_{2z}$$

$$-\frac{3}{4}s^2\theta\, c(2\phi)\left[I_{1+}I_{2+} + I_{1-}I_{2-}\right]$$

$$I_{1z}I_{2z} + \frac{I_{1+}I_{2-}}{2} + \frac{I_{1-}I_{2+}}{2}$$

$$-\frac{3}{4}s^2\theta\left[I_{1+}I_{2-} + I_{1-}I_{2+}\right]$$

$$-\frac{3}{4i}s^2\theta\, s(2\phi)\left[I_{1+}I_{2+} - I_{1-}I_{2-}\right]$$

$$-\frac{3\cos\theta}{2} e^{-i\phi}\left(I_{1+}I_{2z} + I_{1z}I_{2+}\right)$$ Done (C)

$$-\frac{3\cos\theta}{2} e^{i\phi}\left[I_{1-}I_{2z} + I_{1z}I_{2-}\right]$$ Done (D)

$\cancel{\frac{A}{2} \frac{3}{4} s^2\theta \{A\}}$ Work ON $s^2\theta c(2\phi)$ & $s^2\theta s(2\phi)$

$$\frac{s^2\theta c(2\phi)}{4}\left[I_{1+}I_{2+} + I_{1-}I_{2-}\right]$$

$$+\frac{s^2\theta s(2\phi)}{4i}\left[I_{1+}I_{2+} - I_{1-}I_{2-}\right]$$

$$\Rightarrow \cancel{I_{1+}I_{2+}\{} \frac{s^2\theta}{4} I_{1+}I_{2+}\left[c(2\phi)+\frac{s(2\phi)}{i}\right]$$

$$+\frac{s^2\theta}{4} I_{1-}I_{2-}\left[c(2\phi)-\frac{s(2\phi)}{i}\right]$$

$$\boxed{= \frac{s^2\theta}{4} I_{1+}I_{2+}e^{-i2\phi} + \frac{s^2\theta}{4} I_{1-}I_{2-}e^{i2\phi}}$$

$$\Rightarrow \boxed{-\frac{3s^2\theta}{4} I_{1+}I_{2+}e^{-i2\phi} - \frac{3}{4}s^2\theta I_{1-}I_{2-}e^{i2\phi}}$$

DONE (E) DONE (F)

$$\boxed{\hat{H}_D = \frac{\gamma_1 \gamma_2}{r^3}\left[\bar{I}_1 \cdot \bar{I}_2 - \frac{3(\bar{I}_1 \cdot \bar{r})(\bar{I}_2 \cdot \bar{r})}{r^2}\right] =}$$

$$A = I_{1z} I_{2z} (1 - 3c^2\theta)$$

$$B = -\frac{[I_{1+} I_{2-} + I_{1-} I_{2+}]}{4}[1 - 3c^2\theta]$$

$$C = -\frac{3(c\theta)(s\theta)}{2} e^{-i\phi}[I_{1+} I_{2z} + I_{1z} I_{2+}]$$

$$D = -\frac{3(c\theta)(s\theta)}{2} e^{i\phi}[I_{1-} I_{2z} + I_{1z} I_{2-}]$$

$$E = \frac{-3s^2\theta}{4} e^{-i2\phi}[I_{1+} I_{2+}]$$

$$F = \frac{-3s^2\theta}{4} e^{i2\phi}[I_{1-} I_{2-}]$$

$* w_D$

$$\boxed{w_D = \frac{\gamma_1 \gamma_2}{r^3}}$$

$$\boxed{\hat{H}_D = w_D [A + B + C + D + E + F]}$$

HW III, 2 - calculate the matrix elements of the terms in Dipolar alphabet, for a 2-spin system, specify which spin states are connected by each term of D.P. alphabet,

$$I_z = \frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \quad I_+ = \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix} \quad I_- = \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}$$

$$I_x = \frac{1}{2}\begin{pmatrix}0 & 1\\ +1 & 0\end{pmatrix} \quad I_y = \frac{-1}{2}\begin{pmatrix}0 & i\\ -i & 0\end{pmatrix}$$

$$A = A' I_{1z} I_{2z}$$

$$I_+ = I_x + i I_i$$

$$= \frac{1}{2}\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix} + \frac{-i}{2}\begin{pmatrix}0 & i\\ -i & 0\end{pmatrix}$$

$$= \text{''} + \frac{1}{2}\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix}0 & 1\\ +1 & 0\end{pmatrix} \pm \frac{1}{2}\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}$$

$$= (-1$$

$$I_+ = I_x + i I_y$$

$$\Rightarrow i + \left[\frac{-1}{2}\begin{pmatrix}0 & i\\ -i & 0\end{pmatrix}\right)$$

$$= \frac{-1}{2}\begin{pmatrix}0 & i^2\\ -i^2 & 0\end{pmatrix}$$

$$= \frac{-1}{2}\begin{pmatrix}0 & -1\\ 1 & 0\end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix}0 & 1\\ +1 & 0\end{pmatrix} + \frac{1}{2}\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix} = \frac{1}{2}\begin{pmatrix}0 & 2\\ 0 & 0\end{pmatrix} = \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}$$

$$\bar{M} = \gamma \bar{S}$$

$$H = -\bar{M}\cdot\bar{B}$$

$$\bar{B} = B_0 \cdot \hat{z}$$

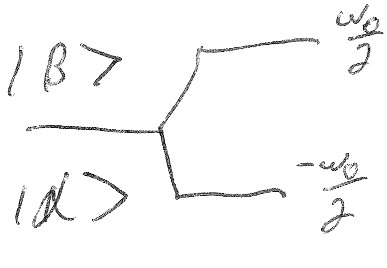
$$H = -\gamma B_0 \cdot \hat{S}_z = \hat{H} = -\omega_0 \hat{S}_z$$

$$S_z = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

$$|\alpha\rangle = \begin{pmatrix}1\\ 0\end{pmatrix}$$

$$|\beta\rangle = \begin{pmatrix}0\\ 1\end{pmatrix}$$

$$\hat{H}_z = -\omega_0\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$



$$\hat{H}_z|\alpha\rangle = -\frac{\omega_0}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix} = \begin{pmatrix}1\\ 0\end{pmatrix}\left(-\frac{\omega_0}{2}\right) = \frac{-\omega_0}{2}|\alpha\rangle$$

$$H_z|\beta\rangle = \frac{-\omega_0}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}0\\ 1\end{pmatrix} = \frac{-\omega_0}{2}\begin{pmatrix}0\\ -1\end{pmatrix} = \frac{\omega_0}{2}|\beta\rangle$$

a) $S_x = \frac{1}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$ $\quad S_z = \frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$ $\quad S_+ = S_x + iS_y$

$S_y = \frac{1}{2}\begin{pmatrix}0 & -i\\ +i & 0\end{pmatrix}$ $\quad S_- = S_x - iS_y$

$$S_+ = \frac{1}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} + \frac{i}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} = \frac{1}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} + \frac{1}{2}\begin{pmatrix}0 & -i^2\\ i^2 & 0\end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} + \frac{1}{2}\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix}0+0 & 1+1\\ 1-1 & 0+0\end{pmatrix} = \frac{1}{2}\begin{pmatrix}0 & 2\\ 0 & 0\end{pmatrix} = \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}$$

$$\boxed{S_+ = \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix} \quad S_- = \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}}$$

$$S_x \cdot S_+ = \frac{1}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix} = \frac{1}{2}\begin{pmatrix}0 & 0\\ 0 & 0\end{pmatrix} = 0$$

$$S_- \cdot S_+ = \begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix} = \begin{pmatrix}0 & 0\\ 0 & 1\end{pmatrix}$$

$$S_+ S_- = \begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix}\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix} = \begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix}$$

	$\alpha\alpha$	$\beta\alpha$	$\alpha\beta$	$\beta\beta$
$\alpha\alpha$				
$\beta\alpha$				
$\alpha\beta$				
$\beta\beta$				

expand for $\alpha\alpha$ $\alpha\beta$ ... basis 4×4

$$A = A' \hat{I}_{1z} \hat{I}_{2z} = A' \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \times \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

$$A = \frac{A}{4} \begin{array}{c} \alpha\alpha \;\; \beta\alpha \;\; \alpha\beta \;\; \beta\beta \\ \begin{pmatrix}1 & 0 & 0 & 0\\ 0 & -1 & 0 & 0\\ 0 & 0 & -1 & 0\\ 0 & 0 & 0 & 1\end{pmatrix}\end{array} =$$

NO TRANSITIONS JUST ROTS

$B = B'(I_{1+}I_{2-} + I_{1-}I_{2+})$ $\qquad$ ~~$I_+ = \frac{1}{2}\begin{pmatrix}0&1\\-1&0\end{pmatrix}$~~

$I_+ = \begin{pmatrix}0&1\\0&0\end{pmatrix} \qquad I_- = \begin{pmatrix}0&0\\1&0\end{pmatrix}$

$$= \begin{pmatrix}0&1\\0&0\end{pmatrix} \times \begin{pmatrix}0&0\\1&0\end{pmatrix} + \begin{pmatrix}0&0\\1&0\end{pmatrix}\begin{pmatrix}0&1\\0&0\end{pmatrix}$$

$$= \begin{matrix}0&0&0&0\\0&0&0&0\\0&1&0&0\\0&0&0&0\end{matrix} + \begin{matrix}0&0&0&0\\0&0&1&0\\0&0&0&0\\0&0&0&0\end{matrix} = \begin{array}{cccc|c}\alpha\alpha&\beta\alpha&\alpha\beta&\beta\beta&\\ \hline 0&0&0&0&\alpha\alpha\\0&0&1&0&\beta\alpha\\0&1&0&0&\alpha\beta\\0&0&0&0&\beta\beta\end{array}$$

$\beta\alpha \to \alpha\beta$

$\alpha\beta \to \beta\alpha$

$C = C'(I_{1z}I_{2+} + I_{1+}I_{2z})$

$$= \frac{C'}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix} \times \begin{pmatrix}0&1\\0&0\end{pmatrix} + \frac{1}{2}\begin{pmatrix}0&1\\0&0\end{pmatrix} \times \begin{pmatrix}1&0\\0&-1\end{pmatrix}$$

$$= \frac{C'}{2}\left[\begin{matrix}0&0&1&0\\0&0&0&-1\\0&0&0&0\\0&0&0&0\end{matrix} + \begin{matrix}0&1&0&0\\0&0&0&0\\0&0&0&-1\\0&0&0&0\end{matrix}\right] = \frac{C'}{2}\begin{array}{c}\begin{array}{cccc}\alpha\alpha&\beta\alpha&\alpha\beta&\beta\beta\end{array}\\ \begin{bmatrix}0&1&1&0\\0&0&0&-1\\0&0&0&-1\\0&0&0&0\end{bmatrix}\end{array}\begin{array}{c}\alpha\alpha\\\beta\alpha\\\alpha\beta\\\beta\beta\end{array}$$

$$D = C^* = \frac{C'}{2}\begin{bmatrix}0&0&0&0\\1&0&0&0\\1&0&0&0\\0&-1&-1&0\end{bmatrix}$$

$\beta\alpha \to \alpha\alpha$

$\alpha\beta \to \alpha\alpha$

$\beta\beta \to \alpha\beta$

$\beta\beta = \alpha\beta$

$$E = E' I_1 + I_{2} +$$

$$= E' \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \times \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} = \begin{array}{c|cccc} & \alpha\alpha & \beta\alpha & \alpha\beta & \beta\beta \\ \hline \alpha\alpha & 0 & 0 & 0 & 1 \\ \beta\alpha & 0 & 0 & 0 & 0 \\ \alpha\beta & 0 & 0 & 0 & 0 \\ \beta\beta & 0 & 0 & 0 & 0 \end{array} \; E'$$

$\alpha\alpha \to \beta\beta$

$$F = E^{*} = E' \begin{array}{cccc|c} \alpha\alpha & \beta\alpha & \alpha\beta & \beta\beta & \\ \hline 0 & 0 & 0 & 0 & \alpha\alpha \\ 0 & 0 & 0 & 0 & \beta\alpha \\ 0 & 0 & 0 & 0 & \alpha\beta \\ 1 & 0 & 0 & 0 & \beta\beta \end{array}$$

$\alpha\alpha \to \beta\beta$

	$\alpha\alpha$	$\beta\alpha$	$\alpha\beta$	$\beta\beta$
$\alpha\alpha$	$\frac{A}{4}$			
$\beta\alpha$		$-\frac{A}{4}$		
$\alpha\beta$			$-\frac{A}{4}$	
$\beta\beta$				$A/4$

	$\alpha\alpha$	$\beta\alpha$	$\alpha\beta$	$\beta\beta$
$\alpha\alpha$	$\frac{A'}{4} + \frac{\Sigma}{2}$	$\frac{C'}{2}$	$\frac{C'}{2}$	E'
$\beta\alpha$	$\frac{D'}{2}$	$\frac{-A}{4} + \frac{\Delta}{2}$	B'	$\frac{-C'}{2}$
$\alpha\beta$	$\frac{D'}{2}$	B'	$\frac{-A'}{4} - \frac{\Delta}{2}$	$\frac{-C'}{2}$
$\beta\beta$	F'	$\frac{-D'}{2}$	$\frac{-D'}{2}$	$\frac{A'}{4} - \frac{\Sigma}{2}$

$\Sigma = -\omega_0^1 - \omega_0^2$

$\Delta = \omega_0^1 - \omega_0^2$

III. 3 Truncation by the Zeeman Hamiltonian: Demonstrate that given two Hamiltonians H_0 (Zeeman usually) & H_1 with $\|H_0\| \gg \|H_1\|$, the energy levels arising from a first order perturbative treatment of H_1 are the same as those obtained by considering a truncated Hamiltonian H_1^T

where

$$H = H_0 + H_1^T$$

$$H_1 = H_1^T + H_1^{nc} \;;\; [H_0, H_1^T] = 0 \;;\; [H_0, H_1^{nc}] \neq 0$$

$$M = \gamma S_z$$

$$H_Z = -\bar{M} \cdot \bar{B}_0 \qquad \therefore H_Z = -\gamma B_0 S_z = -\omega_0 S_z$$

$$\hat{H}_Z = -\omega_0 \hat{S}_Z \qquad S_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$H_1 = \cancel{H_Z} H_D$$

(a) $H_0 = H_Z$ &

$$\hat{A} f = c f$$

$$[A, B] = AB - BA$$

1) calculate $|i\rangle$ of H_Z & express each element of the total Hamiltonian as

$$\hat{H}_0 + H_1^T$$

$$H_{ij} = \langle i | H_Z | j \rangle + \langle i | H_D | j \rangle$$

$$\boxed{H_{ij} = \underbrace{H_{ij}^0}_{\text{unperturbed}} + \langle i | H_D | j \rangle}$$

actually $\boxed{E_{ij} = E_{ij}^0 + \langle i^0 | H_D | j^0 \rangle}$ — ? not

$$\hat{H} = H_0 + H_1 \Rightarrow \hat{H} = H_0 + (H_1^t + H_1^{nc})$$

$$[H_0, H_1^{nc}] \neq 0$$

$$\boxed{[H_0, H_1^t] = 0} \quad H_0 H_1^t - H_1^t H_0 = 0$$

$$E_0 = \Big(\Sigma \langle \alpha | \alpha \rangle + \Delta \langle \alpha | \beta \rangle - \Delta \langle \beta | \alpha \rangle - \Sigma \langle \beta | \beta \rangle$$

$$|i\rangle = |\alpha_1 \alpha_2\rangle,\ |\alpha_2 \beta_2\rangle.$$

$$H = H_0 + H_1^t \qquad \langle j| = \langle \alpha_1 \alpha_2|,\ \langle \alpha_2 \beta_2|$$

$$\delta_{ij} = \langle i | j \rangle$$

$$H_{ij} = \langle i | H_z | j \rangle = H_{ij}^0 =$$

	$\|1\rangle$ $\alpha\alpha$	$\|2\rangle$ $\beta\alpha$	$\|3\rangle$ $\alpha\beta$	$\|4\rangle$ $\beta\beta$
$\alpha\alpha$	Σ			
$\beta\alpha$		Δ		
$\alpha\beta$			$-\Delta$	
$\beta\beta$				$-\Sigma$

$$\Delta = \omega_0^1 - \omega_0^2$$

$$\Sigma = -\omega_0^1 - \omega_0^2$$

$$\langle 1 | H_z | 1 \rangle = \langle \alpha_1 \alpha_2 | -\gamma B_0 S_{z1} - \gamma B_0 S_{z2} | \alpha_1 \alpha_2 \rangle$$

$$\frac{1}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \frac{1}{2}\begin{pmatrix}1\\0\end{pmatrix}$$

$$= -\frac{\omega_0^1}{2} - \frac{\omega_0^2}{2}$$

$$\boxed{H^0\psi^1 - E^0\psi^1 = E^1\psi^0 - H^1\psi^0}$$ ← 1^{st} order

$\langle \psi_n^0 | \psi_n^1 \rangle = 0$
(by normaliz)

1^{st} order E collection

$$E_n \approx E_n^0 + E_n^1 = E_n^0 + \langle \psi_n^0 | \hat{H}^1 | \psi_n^0 \rangle$$

$$E_n = E^0 + \langle i | \hat{H}^1 | j \rangle$$

Homonuc $H = H_z + \omega_0 P_2 (3 I_{1z} I_{2z} - \bar{I}_1 \cdot \bar{I}_2)$ — Kett can't use PT

Het $H = H_z + \omega_0 P_2 (I_{1z} I_{2z})$ — PT works

$A = \omega_D P_2 (I_{1z} I_{2z})$

$A = A'(I_{1z} I_{2z})$

$$\begin{pmatrix} \frac{A'}{2}+\Sigma & & & \\ & \frac{A'}{2}+\Delta & & \\ & & \frac{A'}{2}-\Delta & \\ & & & \frac{A'}{2}-\Sigma \end{pmatrix} = \text{Total Homo}$$

$\Sigma = -\omega_0^1 - \omega_0^2 \approx 100\ MHz$

$\Delta = \omega_0^1 - \omega_0^2 \approx 10\ kHz$ (for H/H)

$\approx$ (MHz) (for H/C)

$\frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix}$

$\langle \alpha | \beta \rangle \to 0$

$\langle \beta | \alpha \rangle \to 0$

$H_z \Rightarrow \langle 1 | \hat{H}_z | 1 \rangle = \langle \alpha_1 \alpha_2 | H_z | \alpha_1 \alpha_2 \rangle =$

$$-\frac{\gamma B_0}{2\pi} \begin{array}{c|cccc} & 1 & 2 & 3 & 4 \\ \hline 1 & S_z & & & \\ 2 & & S_z & & \\ 3 & & & S_z & \\ 4 & & & & S_z \end{array} \Rightarrow \begin{pmatrix} +\omega_{01} + \omega_{02} & & & \\ & \Delta & & \\ & & -\Delta & \\ & & & -\Sigma \end{pmatrix}$$

$\therefore \quad \psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots \lambda^k \psi_n^{(k)}$

$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots \lambda^k E_n^{(k)}$

orthogonal corrections to wave func

require $\langle \psi_n^{(0)} | \psi_n \rangle = 1$ (normalized)

$1 = \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + \lambda \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \lambda^2 \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \cdots$

$\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1 \quad \therefore \quad \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle = 0$ etc

---

$\cancel{H\psi_n = (H^0 + \lambda)\psi_n} \qquad H\psi_n = (H^0 + \lambda H')\psi_n$

$= (H^0 + \lambda H')(\psi_n^0 + \lambda \psi_n' + \lambda^2 \psi_n^2 + \cdots) = (E_n^0 + \lambda E_n' + \lambda^2 E_n^2 + \cdots)(\psi_n^0 + \lambda \psi_n' + \lambda^2 \psi_n^2 + \cdots)$

collect like λ's

$H^0 \psi_n^0 + \lambda(H' \psi_n^0 + H^0 \psi_n') + \lambda^2 (H^0 \psi_n^2 + H^0 \psi_n^2) + \ldots$

$= E_n^0 \psi_n^0 + \lambda(E_n' \psi_n^0 + E_n^0 \psi_n') + \lambda^2 (E_n^2 \psi_n^0 + E_n' \psi_n' + E_n^0 \psi_n^2) + \ldots$

~~λ^0: $H^0 \psi_n^0 = E_n^0 \psi_n^0$~~

~~λ': $H' \psi_n^0 = E_n' \psi_n^0$~~

~~$H^0 \psi_n' = E_n^0 \psi_n'$~~

λ^0: $H^0 \psi_n^0 = E_n^0 \psi_n^0$

λ': $H' \psi_n^0 + H^0 \psi_n' = E_n' \psi_n^0 + E_n^0 \psi_n'$

$H^0 \psi_n' - E_n^0 \psi_n' = E_n' \psi_n^0 - H' \psi_n^0$

1st order correction

$$\boxed{H^0 \psi' - E^0 \psi' = E' \psi^0 - H' \psi^0}$$ start here

Perturbation Theory $\hat{H}\Psi = E\Psi$

$\hat{H}^0 \psi_n^0 = E_n^0 \psi_n^0$ (very close to orig)

$\hat{H}\Psi = E\Psi$

$\cancel{\hat{H}^0\psi^0 = E^0\psi^0}$

~~here~~ * λ = scaling factor for smooth transit

$\hat{H} = \hat{H}^0 + \hat{H}'$

or $\hat{H}' = \hat{H} - \hat{H}^0$

$$\boxed{\hat{H} = \hat{H}^0 + \lambda \hat{H}'}$$

Non-degenerate PT (unique e-levels for all)

$$\hat{H}_\lambda \psi_n = (\hat{H}^0 + \lambda \hat{H}')\psi_n = E_n \psi_n$$

$\psi_n = \psi_n(\lambda, q)$ $E_n = E_n(\lambda)$

ef & ev depend on λ (q = coords x, y, z)..

expand ψ_n & E_n via Taylor series

$$\psi_n = \psi_n\Big|_{\lambda=0} + \frac{\partial \psi_n}{\partial \lambda}\Big|_{\lambda=0}\left(\frac{\lambda}{1!}\right) + \psi_n\Big|_{\lambda=0}\frac{\partial^2 \psi_n}{\partial \lambda^2}\left(\frac{\lambda^2}{2!}\right) + \ldots$$

$$E_n = E_n\Big|_{\lambda=0} + \frac{dE_n}{d\lambda}\Big|_{\lambda=0}\left(\frac{\lambda}{1!}\right) + \frac{d^2E_n}{d\lambda^2}\Big|_{\lambda=0}\left(\frac{\lambda^2}{2!}\right) + \ldots$$

@ $\lambda = 0$ $\psi_n\Big|_{\lambda=0} = \psi_n^{(0)}$ $E_n\Big|_{\lambda=0} = E_n^{(0)}$

abbrev (bleeus!)

$$\psi_n^{(k)} = \frac{1}{k!}\frac{\partial^k \psi_n}{\partial \lambda^k}\Big|_{\lambda=0}$$

$$E_n^{(k)} = \frac{1}{k!}\frac{d^k E_n}{d\lambda^k}\Big|_{\lambda=0}$$

II-4 calculate the x, y, z components of the total angular momentum, F, for a 2-spin 1/2 particle. Show that these components fulfill the commutation relationships for angular momentum

$I_x = \frac{I_+ + I_-}{2}$ $\quad I_y = \frac{I_+ - I_-}{2i}$ $\quad S_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$I_+ = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$ or $S_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ $\quad S_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$

*need to expand to $|\alpha\alpha\rangle, \ldots$ basis

$F_z = I_{z1} + I_{z2} \Rightarrow I_{z1} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

$I_{z2} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$I_{z1} = \begin{matrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{matrix}$ $\quad I_{z2} = \begin{matrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{matrix} \Rightarrow F_z = \frac{1}{2}\begin{bmatrix} 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2 \end{bmatrix}$

$F_z = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$

$F_x = I_{1x} + I_{2x}$ $\quad I_{1x} = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

$= \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

$= \begin{matrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{matrix} + \begin{matrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{matrix} \Rightarrow F_x = \frac{1}{2}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix}$

$F_y = I_{1y} + I_{2y}$ $\qquad I_{1y} = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$

$$= \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\frac{1}{2}\begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix} + \frac{1}{2}\begin{pmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{pmatrix} = \frac{i}{2}\begin{pmatrix} 0 & -1 & -1 & 0 \\ 1 & 0 & 0 & -1 \\ 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \end{pmatrix} = F_y$$

$$F^2 = \frac{3}{4}\hbar^2 \mathbb{1}$$

$$F_z F_x - F_x F_z = \frac{1}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & & \\ & & 0 & \\ & & & -1 \end{pmatrix}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix} - \frac{1}{2}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix}\begin{pmatrix} 1 & & & \\ & 0 & & \\ & & 0 & \\ & & & -1 \end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix} 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & -1 & -1 & \end{pmatrix} - \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & -1 \\ 1 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 1 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & -1 & 0 \end{pmatrix}\frac{1}{2} = -\frac{1}{2i} I_y = \frac{i I_y}{2}$$

$\{ S_x, S_y, S_z \}$

$$[S_i, S_j] = i\,\epsilon_{ijk} S_k$$

$$[S_j, S_i] = -i\,\epsilon_{ijk} S_k$$

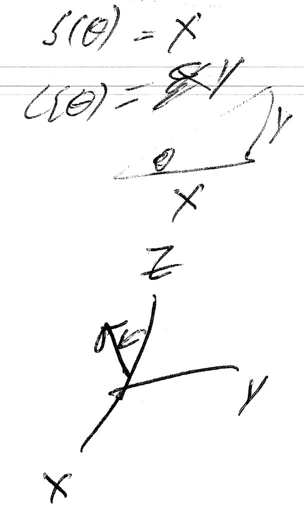
$[S_x, S_y] = i S_z$

$[S_y, S_z] = i S_x$

$[S_z, S_x] = i S_y$

$$\epsilon_{ijk} = \begin{cases} 1 & i,j,k = x,y,z \\ -1 & \text{otherwise} \end{cases}$$

III.5 NMR signal of several coupled spins (1)



$$\rho_{eq} = \underbrace{\cancel{1}}_{\text{triv}} + a_z I_z \propto I_z$$

After pulse: $\beta = \omega_1 \tau$ along X

$$\rho(\tau) = e^{i\omega_1 \tau I_x} \rho_{eq}\, e^{-i\omega_1 \tau I_x}$$

$$= \underbrace{a_z (\cos(\beta) I_z}_{\text{Not detected along } -z} - \sin(\beta)\cdot I_y)$$

Now evolve under $\vec{H}$

$$\boxed{\rho(t) = e^{-iHt} \rho(\tau)\, e^{iHt}}$$

$$S_+(t) = I_x + iI_y = I_+ \quad \text{(Detect signal)} \qquad I_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$s(t) = \mathrm{Tr}\left[\rho(t)\cdot I_+\right]$$

Pauli 1-spin

$$I_{z_1} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Now need 2-spin description

2^n = dimensionality

2-spins $|\alpha\alpha\rangle, \ldots$

$$I_{z1} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \otimes \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}}_{\mathbb{1}}$$

$$= \frac{\hbar}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} = I_{z1}$$

$$I_{z2} = \underbrace{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}}_{\mathbb{1}\ \text{(note order)}} \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

Total Angulalar mom.

$$F_z = I_{z1} + I_{z2} = \frac{\hbar}{2}\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2 \end{pmatrix} = \hbar\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

2-spin raising operator (Detect signal)

1-spin $I_{1+} = \begin{array}{c|cc} & \alpha & \beta \\ \alpha & 0 & 1 \\ \beta & 0 & 0 \end{array}$ $\alpha \to \beta$

$$F_+ = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$= \frac{\hbar}{2}\begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix} + \frac{\hbar}{2}\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} = \hbar \begin{array}{c} \begin{array}{cccc} 1 & 2 & 3 & 4 \end{array} \\ \begin{pmatrix} 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix} \end{array} \begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \end{array}$$

$\therefore$ ~~$F_+ \to \rho$~~ $\mathrm{Tr}\,[\rho(t) \cdot F_+)$

$$\boxed{\mathrm{Tr}\,(\rho(t) \cdot F_+) = \rho_{21}(t) + \rho_{31}(t) + \rho_{42}(t) + \rho_{43}(t)}$$

2-spin transitions

ρ of states w/ $\Delta M = \pm 1$)

IN TOTAL DIP Hamil MATRIX

$$H = \frac{1}{2} \cdot \begin{array}{c|cccc} & \alpha\alpha & \beta\alpha & \alpha\beta & \beta\beta \\ \hline \alpha\alpha & \frac{A'}{2}+\Sigma & C' & C' & 2E' \\ \beta\alpha & D' & \frac{A'}{2}+\Delta & \cancel{\frac{A'}{2}+\Delta}\ 2B' & C' \\ \alpha\beta & D' & 2B' & \frac{A'}{2}-\Delta & C' \\ \beta\beta & 2F' & D' & D' & \frac{A'}{2}-\Sigma \end{array}$$

$\cancel{\Sigma = \frac{\omega_{01}}{2}}\ \omega.$ $\Sigma = -\omega_{01} - \omega_{02}$

$\Delta = \omega_{01} - \omega_{02}$

$\Sigma \cdot \alpha\ 100\,MHz$

$\Delta\ \alpha\ DIP\ \alpha\ 10\,kHz$

---

2 cases arise

Homo Nuc

$|\Delta| \simeq |\omega_D|$

$H = H_Z + \omega_D (A + B)$

$$\boxed{H = H_Z + \omega_D \cdot P_2 \cdot (3 I_{1z} I_{2z} - \vec{I}_1 \cdot \vec{I}_2)}$$

$\vec{I}_1 \cdot \vec{I}_2 = I_{1x} I_{2x}\ I_{1y} I_{2y} + I_{1z} I_{2z}$

$= I_{1z} I_{2z} + \frac{1}{2}(I_{1+} I_{2-} + I_{1-} I_{2+})$

Hetero Nuc

$|\Delta| >> |\omega_D|$

$H = H_Z + \omega_D \cdot A$

$$\boxed{H = H_Z + \omega_D \cdot P_2 \cdot I_{1z} I_{2z}}$$

$|2\rangle = |\alpha\alpha, \beta\alpha\rangle$ $\qquad H_Z = \frac{-\omega_{01}}{2} I_{z_1} - \frac{\omega_{02}}{2} I_{z_2}$

$$\langle \alpha_1 \alpha_2 | H | \beta_1 \alpha_2 \rangle = \langle \alpha_1 \alpha_2 | -\frac{\omega_0}{2} I_{z_1} - \omega_0 I_{z_2} + H_D | \beta_1 \alpha_2 \rangle$$

$$\langle \alpha_2 | \alpha_2 \rangle \cancel{\langle \alpha_1 | -\omega_0 I_{z_1} | \beta_1 \rangle} \to 0 + \langle \alpha_2 | -\omega_0 I_{z_1} | \alpha_2 \rangle \cancel{\langle \alpha_1 | \beta_1 \rangle} \to 0 + DIP$$

$\boxed{B_0 \uparrow \quad \uparrow \alpha \quad \downarrow \beta}$

$H_Z \to 0$

$I_+ |\alpha\rangle = 0$

$I_+ |\beta\rangle = |\alpha\rangle$

$I_- |\alpha\rangle = |\beta\rangle$

$I_- |\beta\rangle = 0$

DIP $\quad \langle \alpha_1 \alpha_2 | H_D | \beta_1 \alpha_2 \rangle =$

$$B^* = B' \cdot (I_{1+} I_{2-} + I_{1-} I_{2+})$$

$$\langle \alpha_1 \alpha_2 | B | \beta_1 \alpha_2 \rangle = \langle \alpha_1 \alpha_2 | I_{1+} I_{2-} + I_{1-} I_{2+} | \beta_1 \alpha_2 \rangle$$

$$= \langle \alpha_1 \alpha_2 | I_{1+} I_{2-} | \beta_1 \alpha_2 \rangle + \langle \alpha_1 \alpha_2 | I_{1-} I_{2+} | \beta_1 \alpha_2 \rangle$$

$$= \langle \alpha_1 | \beta_1 \rangle \cdot \cancel{\langle \alpha_2 | I_{2-} | \alpha_2 \rangle} \to 0 \cdot \langle \alpha_1 | I_{1-} | \beta_1 \rangle \cdot \cancel{\langle \alpha_2 | I_{2+} | \alpha_2 \rangle} \to 0$$

NOT B' for $\cancel{|2\rangle}$ $\quad |\alpha_1 \alpha_2, \beta_2 \alpha_1\rangle$

$C = C' \cdot (I_{1z} I_{2+} + I_{1+} I_{2z})$

$|\alpha_1 \alpha_2, \beta_1 \alpha_2\rangle$

$\langle \alpha_1 \alpha_2 | H_D | \beta_1 \alpha_2\rangle =$

$= \langle \alpha_1 \alpha_2 | I_{1z} I_{2+} + I_{1+} I_{2z} | \beta_1 \alpha_2\rangle$

$= \langle \alpha_1 \alpha_2 | I_{1z} I_{2+} | \beta_1 \alpha_2\rangle + \langle \alpha_1 \alpha_2 | I_{1+} I_{2z} | \beta_1 \alpha_2\rangle$

$= \langle \alpha_1 | I_{1z} | \beta_1\rangle^{0} \cdot \langle \rangle + \langle \alpha_1 | I_{1+} | \beta_1\rangle \langle \alpha_2 | I_{2z} | \alpha_2\rangle$

$= \langle \alpha_1 | \alpha_1\rangle \cdot \langle \alpha_2 | \alpha_2\rangle \cdot \frac{1}{2}$

$\uparrow \alpha \quad \downarrow \beta$

$\therefore \boxed{H_{21} = \frac{1}{2} \cdot C'}$

$I_+ |\alpha\rangle = 0$

$I_- |\alpha\rangle = |\beta\rangle$

$I_+ |\beta\rangle = |\alpha\rangle$

$I_- |\beta\rangle = 0$

~~$C' = -\frac{3W_D}{4} \sin^2\theta$~~

$C' = -\frac{3W_D}{2} c(\theta) s(\theta) e^{-i\phi}$

$H_z = -w_{0_1} I_{z_1} - w_{0_2} - I_{z_2}$

$$H_{33} = \langle \alpha_1 \beta_2 | H_z + H_D | \alpha_1 \beta_2 \rangle$$

$$= \langle \alpha_1 \beta_2 | -w_{01} I_{z_1} | \alpha_1 \beta_2 \rangle + \langle \alpha_1 \beta_2 | -w_{02} I_{z_2} | \alpha_1 \beta_2 \rangle + \langle \,| H_D | \,\rangle$$

$$= \langle \beta_2 | \beta_2 \rangle \langle \alpha_1 | w_{01} I_{z_1} | \alpha_1 \rangle + \langle \alpha_1 | \alpha_1 \rangle \langle \beta_2 | -w_{02} I_{z_2} | \beta_2 \rangle +$$

$$= \frac{-w_{01}}{2} + \frac{w_{02}}{2} + DIP$$

DIP $\quad I_+ I_- \to 0 \quad \therefore A$ term only

$$\langle \alpha_1 \beta_2 | A' I_{1z} I_{2z} | \alpha_1 \beta_2 \rangle$$

$$= A' \cdot \langle \alpha_1 | I_{1z} | \alpha_1 \rangle \langle \beta_2 | I_{2z} | \beta_2 \rangle$$

$$= A' \cdot \frac{1}{2} \cdot -\frac{1}{2} = -\frac{A'}{4}$$

$$\cancel{H_{33} = -\left(\frac{w_{01}}{2} - \frac{w_{02}}{2}\right) + \frac{A'}{4} = -\frac{1}{2}\left(\Delta + \frac{A'}{2}\right)}$$

$$H_{33} = -\frac{w_{01}}{2} + \frac{w_{02}}{2} - \frac{A'}{4} = -\frac{1}{2}\left[\Delta + \frac{A'}{2}\right)$$

$S(t) = Tr\left[\rho(t)\cdot F_+\right]$

$\boxed{F_+^{m''m} = \langle m''|F_+|m\rangle}$

$\boxed{HW\ III-6}$ $HW\ III-6$

$$F_+ = \begin{pmatrix} 0 & 1 & 1 & 0 \\ & 0 & & 1 \\ & & & 1 \\ & & & 0 \end{pmatrix}\frac{\hbar}{2}$$

$A_{mm''} = \rho_{mm''}(\tau)\cdot F_+^{m''m}$

$\frac{\pi}{2} \Rightarrow -F_Y^{m''m} = -\left(\frac{F_+^{m''m} - F_-^{m''m}}{2i}\right) = \rho_{mm''}$

$A_{mm''} = \frac{-1}{2i}\left[F_+^{mm''} - F_-^{mm''}\right]\cdot\left[F_+^{m''m}\right]$

$= \frac{-1}{2i}\left\{\left[F_+^{mm''}\cdot F_+^{m''m}\right] - \left[F_-^{mm''}\cdot F_+^{m''m}\right]\right.$

Note $F_+^{mm''}\cdot F_+^{m''m} = 0$; since either one must $= 0$ * No, just $I_+\cdot I_+ = 0$

$S_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$ $S_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$ & $I_-\cdot I_+ = \hbar^2\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$

$A_{mm''} = \frac{1}{2i}\left[F_-^{mm''}\cdot F_+^{m''m}\right]$

note $F_-^{mm''} = \left(F_+^{m''m}\right)^*$ $F_+^{mm''} = \langle m|F_+|m''\rangle$

$\therefore A_{mm''} = \left|\left(F_+^{m''m}\right)^2\right|$

$S(\beta)$: Pulse: $\rho(\tau) = e^{i\omega_1\tau I_y}\rho_{eq}\, e^{-i\omega_1\tau I_y} = a_z(\underbrace{c\beta I_z}_{\text{Not Detected}} - s\beta I_x)$

$= S(\beta) I_x$

$\therefore$ $\boxed{A_{mm''} = \frac{+S(\beta)}{2i}\left|F_+^{m''m}\cdot F_+^{m''m}\right|}$

IV - 7

$$H = \begin{pmatrix} \varepsilon + \omega_D - \lambda & & & \\ & \Delta - \omega_D - \lambda & -\omega_D & \\ & -\omega_D & -\Delta - \omega_D - \lambda & \\ & & & -\varepsilon + \omega_D - \lambda \end{pmatrix}$$

$\varepsilon = -\omega_{01} - \omega_{02}$
$= -\omega_0 \quad (-2\omega_D i)$

$\Delta = \omega_{01} - \omega_{02} = 0$

* Watch notes Δ min. than ~~notes~~ HW have wrong sign on B terms

$$\begin{vmatrix} -\omega_D - \lambda & -\omega_D \\ -\omega_D & -\omega_D - \lambda \end{vmatrix} = 0$$

$(-\omega_D - \lambda)(-\omega_D - \lambda) - (-\omega_D)^2$

$\omega_D^2 + 2\omega_D\lambda + \lambda^2 - \omega_D^2$

$\lambda^2 + 2\omega_D \lambda = 0$

$\lambda = 0, -2\omega_D$

$\lambda = 0$:
$$\begin{pmatrix} -\omega_D - 0 & -\omega_D \\ -\omega_D & -\omega_D - 0 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$0 = -\omega_D c_1 - \omega_D c_2 \Rightarrow c_1 = -c_2$

$c_1^2 + c_2^2 = 1 \quad \therefore c_1 = \frac{1}{\sqrt{2}};\ c_2 = -\frac{1}{\sqrt{2}}$

$EV = 0 \qquad ES = \frac{|\alpha\beta\rangle - |\beta\alpha\rangle}{\sqrt{2}}$

$\lambda = -2\omega_D$:
$$\begin{pmatrix} -\omega_D - (-2\omega_D) & -\omega_D \\ -\omega_D & -\omega_D - (-2\omega_D) \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$$\begin{pmatrix} \omega_D & -\omega_D \\ -\omega_D & \omega_D \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

$c_1\omega_D - c_2\omega_D = 0$

$c_1 = c_2$

$c_1^2 + c_2^2 = 1 \ \therefore$

$c_1 = \frac{1}{\sqrt{2}} = c_2$

$EV = -2\omega_D \qquad ES = \frac{|\alpha\beta\rangle + |\beta\alpha\rangle}{\sqrt{2}}$

$\lambda = \omega_0 + \omega_D$

$\lambda = -\omega_0 + \omega_D$

$\omega_0 + \omega_D \quad |\beta\beta\rangle \quad |4\rangle$

$0 \text{ (SINGLET)} \quad (|\alpha\beta\rangle - |\beta\alpha\rangle)/\sqrt{2} \quad |3\rangle$

$-2\omega_D \quad (|\alpha\beta\rangle + |\beta\alpha\rangle)/\sqrt{2} \quad |2\rangle$

$-\omega_0 + \omega_D \quad |\alpha\alpha\rangle \quad |1\rangle$

$\leftarrow \frac{3\omega_D}{2} \rightarrow$

$1.5\omega_D \quad 1.5\omega_D$

ω_0

$\nu_{12} = -2\omega_D - (-\omega_0 + \omega_D) = \omega_0 + 3\omega_D$

$= -2\omega_D + \omega_0 - \omega_D$

$\checkmark$ Factor of 2 in H prefix $\frac{1}{2}(\;)$

Transition $\boxed{\text{Amplitudes} = |\langle i|F_+|j\rangle|^2}$

$$\boxed{\begin{aligned} |1\rangle &= (1000) \\ |2\rangle &= (0110)\times\left(\tfrac{1}{\sqrt{2}}\right) \\ |3\rangle &= (01\text{-}10)\left(\tfrac{1}{\sqrt{2}}\right) \\ |4\rangle &= (0001) \end{aligned}}$$

$\langle 1|$ really

$$A_{12} = (1000)\begin{pmatrix}0&1&1&0\\0&0&0&1\\0&0&0&1\\0&0&0&0\end{pmatrix}\begin{pmatrix}0\\1\\1\\0\end{pmatrix}\frac{1}{\sqrt{2}}$$

$$= (1000)\begin{pmatrix}2\\0\\0\\0\end{pmatrix} = \left(\frac{2}{\sqrt{2}}\right)^2 = 2$$

$$A_{13} = (1000)\begin{pmatrix}0&1&1&0\\0&0&0&1\\0&0&0&1\\0&0&0&0\end{pmatrix}\begin{pmatrix}0\\1\\-1\\0\end{pmatrix}\frac{1}{\sqrt{2}} = (1000)\begin{pmatrix}0\\0\\0\\0\end{pmatrix} = 0$$

$$A_{24} = (0110)\begin{pmatrix}0&1&1&0\\0&0&0&1\\0&0&0&1\\0&0&0&0\end{pmatrix}\begin{pmatrix}0\\0\\0\\1\end{pmatrix}\times\frac{1}{\sqrt{2}} = (0110)\begin{pmatrix}0\\1\\1\\0\end{pmatrix} = \left(\frac{2}{\sqrt{2}}\right)^2 = 2$$

$A_{12} = A_{21} = 2$

$A_{13} = A_{14} = A_{23} = A_{34} = 0$

$$\frac{2^n(2^n-1)}{2} = \text{\# of Transitions}$$

$$\frac{2^2(3)}{2} = 6$$ ✓

$\underline{\text{III}-8}$

$\langle H_D \rangle = W_D \langle 1 - 3c^2\theta \rangle$, spin

* Jacobi method?

$$= \int_0^{2\pi} \left[\int_0^{\pi} (1-3c^2\theta)\, s\theta\, d\theta \right] d\phi$$

$x = c\theta \quad dx = -s\theta\, d\theta$

$$-\int_0^{\pi} (1-3x^2)\, dx$$

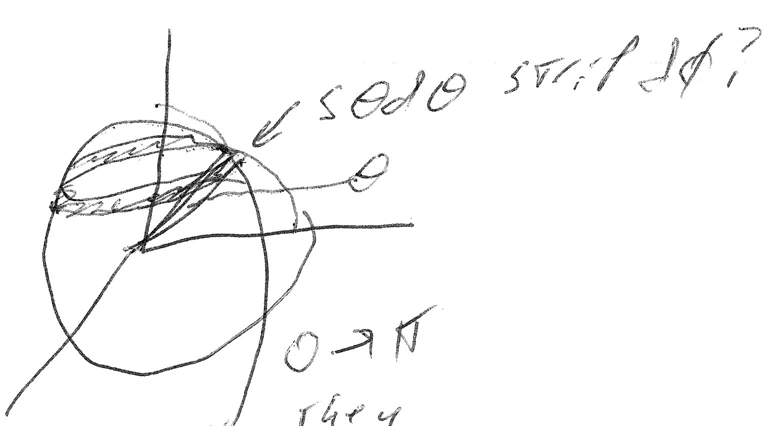
$$\int_{\pi}^{0} (1-3x^2)\, dx = x - x^3 \Big|_{\pi}^{0}$$

$$(c\theta - c^3\theta)\Big|_{\pi}^{0} = c(0) - c^3(0) - [c(\pi) - c^3\pi]$$

$$= 1 - 1 - [-1 - (-1)^3]$$

$$= 0 - [-1 + 1] = 0$$

$$\therefore \int_0^{2\pi} [0]\, d\phi = 0$$



$0 \to \pi$
then
$0 \to 2\pi$
$\Rightarrow$ whole sphere

II-8) demonstrate the angular part of ~~dipole coupling~~ averages to ~~zero upon isotropic~~ tumbling

$W_0 = \gamma B_0$

	$\gamma_N/2\pi$ (MHz/T)
^1H	42.576
^{13}C	10.705
^{31}P	17.235

spin	ν_0 MHz	$\Delta\nu$ Hz	δ (ppm)
^1H (7T)	300	300	1
^{13}C 2.35T	25	2500	100
^1H 11.7T	500.4	5000	10
^{31}P @ 11.7T	201	1069	5.3
^1H @ 11.7T	500.4	2500	5.3

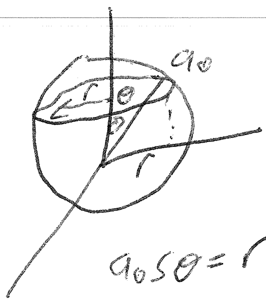
7T × 42.576

III-9 | OK

@ max area $\theta = \frac{\pi}{2}$

$\sigma \approx \mu_{IND}$

$e = 1.6 \times 10^{-19}$ Coulombs



$$\boxed{\mu_{IND} = \left(\frac{e^2}{4 m_e}\right) \cdot B_0 \, a_0^2 \sin^2\theta}$$

$M_e = 9.1 \times 10^{-31}$ kg

$a_0 \sin\theta = r$

$$\mu_{IN} = \frac{(1.6 \times 10^{-19})^2}{9.1 \times 10^{-31}} = B_0 \frac{2.6 \times 10^{-38}}{9.1 \times 10^{-31}} \approx 10^{-6} \cdot B_0$$

$a_0 = 1$

III-10

SPIN (Tesla)	ν_0 (MHz)	$\Delta\nu$ (Hz)	δ (ppm)
^1H @ 7T	300	300	1
^{13}C @ 2.35	25	2500	100
^1H @ 11.7T	500.4	5004	10
^{31}P @ 11.7	202.6	1070	5.3
^1H @ 11.7	500.4	2646	5.3

	^1H	^{13}C	^{31}P
γ_N (MHz/Tesla)	42.576	10.705	17.235

$\omega = -\gamma B_0$

III-12 ^1H = 10 ppm   Resolution Allowed

i) ^{13}C = 200 ppm

$$R = \frac{\text{total freq disp (Hz)}}{\text{fwhh of peak (Hz)}}$$

$H_{lw} \approx 4\, {}^{13}C_{lw}$

<u>100 mHz. Spec</u>

$$R_H = \frac{10 * 100}{4} = \frac{1000}{4} = 250$$

$$R_C = \frac{200 * 25}{\cancel{4}\,1} = \cancel{1250}\ 5000$$

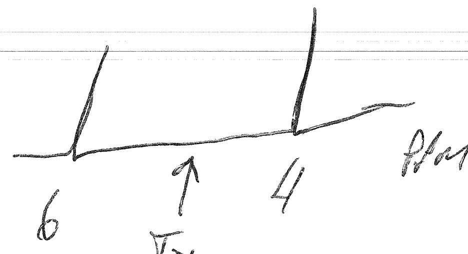
---

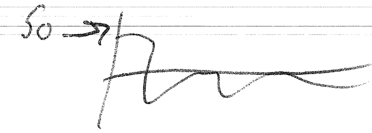
ii) 2 $\frac{5000}{250} \Rightarrow 20$ Times so needed on ^1H

@ 25 mHz = $10 * 2 * 25$ = 500 MHz NMR (11.7 T)

III-13   300 MHz 'H

$$S_0 e^{i\omega t} = [c(\omega t) + i s(\omega t)] S_0$$

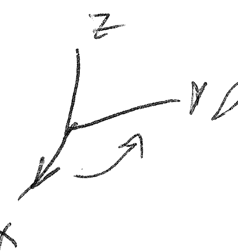




$$S(t) = M_A e^{i\omega_a t} + M_B e^{i\omega_b t}$$

SW = 12 ppm

$m_A = m_B = \hat{x}$



SW = 12 ppm × 300 = 3600 Hz

$\Delta t = \frac{1}{SW} = \frac{1}{3600} = 278\,\mu s$

$W_A = 300(4-5) = -300\,Hz$

$W_B = 300(6-1) = 300$

Let $m_a = m_b = \hat{x}$

$$e^{-i\omega t} + e^{i\omega t} = 2c(\omega t)$$

$$S(t) = S_0 \left[e^{i(\omega_a)\cdot N\cdot\Delta t} + e^{+i\omega_b\cdot(N\cdot\Delta t)} \right]$$

$$\sum_{N=0}^{N-1} S_N(t) = S_0\, e^{i(-300)\cdot N\cdot 278\mu s} + e^{i(300)\cdot N\cdot(278\mu s)}$$

$$\sum_{n=0}^{N-1} S_N = S_0 \left[e^{iN(-8.33e^{-2})\cancel{\times 2\pi}} + e^{iN(-8.33e^{-2})\cancel{\times 2\pi}} \right]$$

$$= \cancel{S_0 \left[e^{(-0.52)iN} + e^{iN(0.52)} \right]} = \cancel{2}$$

$\cancel{\text{Let}}$
$X = (0.52N)$

$$\cancel{= S_0 [2c(0.52\cdot N)]}$$

$$\boxed{\sum_{n=0}^{N-1} 2e^{in(0.083)}}$$

MINS Soln IS wrong mixes up rads

~~E Vals~~ ~~E States Vals~~ ~~Transitions~~

$$\sum_{n=0}^{n-1} S_n \cancel{S(t)} = S_0 [2 \cdot C(0.52 \cdot N)] = 2 \qquad e^{-i\omega t} + e^{i\omega t} = 2C(\omega t)$$

$n=0 \Rightarrow S_0 [2 \cdot C(0)] = 2$

$n=1 \Rightarrow 2 \cdot C(0.52 \cdot 1) = \cancel{1.93} = 1.99$

$2\pi = \frac{6.28\ rad}{S}$

$n=3 \Rightarrow 2\ C(1.5) =$

$\omega = \frac{rad}{S \cdot 2\pi} = \frac{cycle}{S}$

$S_N = \cancel{2 \cdot C}$ $\qquad 2C(0.0833 \cdot N)$

~~$2C(N \cdot 0.0133)$~~

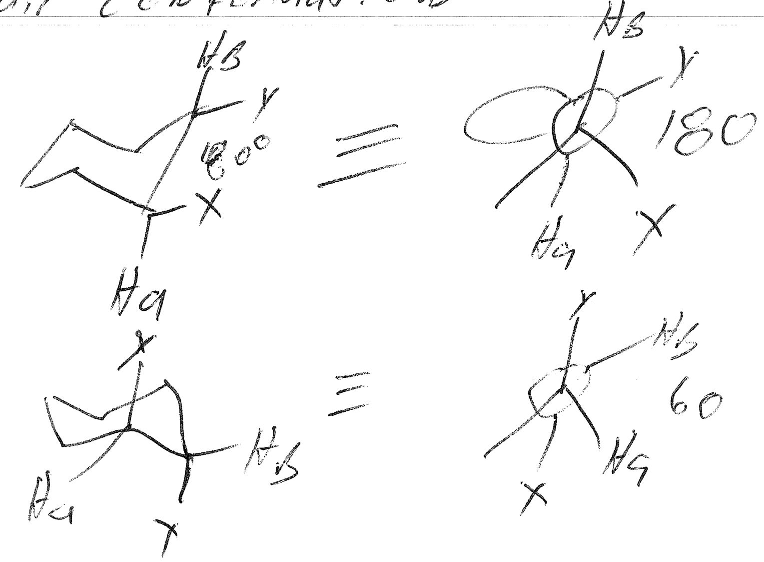
$0 \Rightarrow 2$

$C(X)/2$	degrees $N \cdot 0.0833$	N
	0.0833	1
9.99×10^{-1}	1.66×10^{-1}	2
9.99×10^{-1}	2.49×10^{-1}	3
9.99×10^{-1}	3.32×10^{-1}	4
9.99×10^{-1}	4.15×10^{-1}	5
9.99×10^{-1}	4.98×10^{-1}	6
	5.81×10^{-1}	7
9.99×10^{-1} ~~9.932~~	6.64×10^{-1}	8

* Note, close to on resonance here

Only evolves ½ degree!

III-14) $^3J_{HH}$ coupling constants measured in cyclohexanes are usually the avg of 2 ^3J, each w/a different chair conformation



i) estimate $^3J_{Ha,Hb}$ for each conformation

$$^3J_{HH} = 7 - c(\theta) + 5c(2\theta) \quad [Hz]$$

$$^3J(\theta=180) \Rightarrow 7 - c(180) + 5c(360) =$$

$$7 + 1 + 5 = 13\ Hz$$

$$^3J(\theta=60) = 7 - c(60) + 5c(120)$$

$$= 7 - 0.5 + 5(-0.5)$$

$$= 7 - 0.5 - 2.5 = 4$$

---

ii) $^3J_{HH} = 7Hz$ estimate pops of conformer

$X_1 + X_2 = 1$

$\therefore X_1 = 1 - X_2$

$$J_{obs} = X_1(4) + X_2(13)$$

$$7 = 4X_1 + (1-X_1)13$$

$$7 = 4X_1 + 13 - 13X_1$$

$$-6 = -9X_1$$

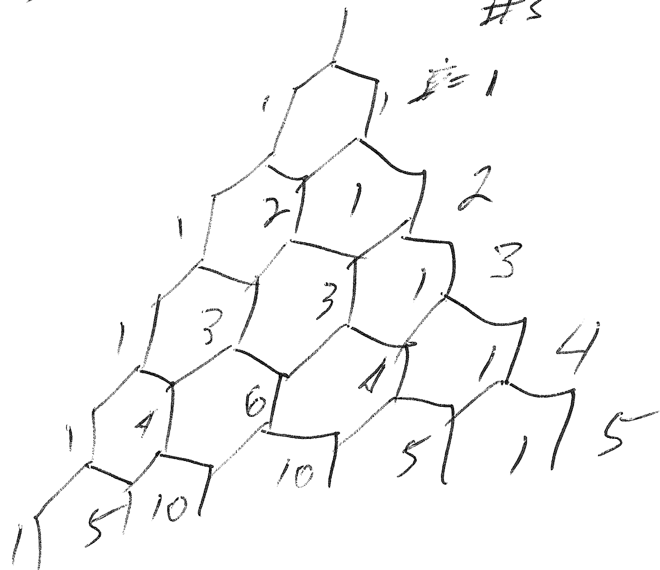
$X_1 = \frac{2}{3}$ $(\theta = 60)$

$X_2 = 1/3$ $(\theta = 180)$

III-15) –

III-16) First order multiplets; what are the relative peak intensities of the multiplets from spin I-5

#5



$2nI+1$

$2(\frac{1}{2})\cancel{5}+1 = 6$ pks

$\boxed{2nI+1}$ – pks

III - 17

$$\cancel{m' = \sum_{m \neq n} \frac{\langle m|H|n\rangle}{E_m - E_n} +}$$

$$\boxed{|n\rangle' = |n\rangle^0 + J \sum_{m \neq n} \frac{\langle m|H'|n\rangle^0}{E_n - E_m} |m\rangle^0}$$

$$|\alpha\beta\rangle' = |\alpha\beta\rangle^0 + J \sum \frac{\left\langle \begin{matrix}\beta\alpha \\ \alpha\alpha \\ \beta\beta\end{matrix} \right| \bar{I}_1 \cdot \bar{I}_2 \left| \alpha\beta \right\rangle^0}{E_* - E_{\alpha\beta}} \left| \begin{matrix}\beta\alpha \\ \alpha\alpha \\ \beta\beta\end{matrix} \right\rangle$$

$$J\, \bar{I}_1 \cdot \bar{I}_2 = \left[I_{1z} I_{2z} + \frac{I_{1-} I_{2+} + I_{1+} I_{2-}}{2} \right] J$$

* not $I_{1z} I_{2z} = 0$ because of $\sum_{n \neq m}$

$$|\alpha\beta\rangle' = |\alpha\beta\rangle^0 + \frac{1}{2} J \left[\cancel{\frac{\langle \beta\alpha | I_{1+} I_{2-} | \alpha\beta\rangle^0}{E_{\beta\alpha} - E_{\alpha\beta}}}^{\,0} + \frac{\langle \beta\alpha | I_{1-} I_{2+} | \alpha\beta\rangle^0}{E_{\beta\alpha} - E_{\alpha\beta}} \right] |\beta\alpha\rangle^0$$

$$|\alpha\beta\rangle' = |\alpha\beta\rangle^0 + \frac{1}{2} J \left[\frac{1}{E_{\beta\alpha} - E_{\alpha\beta}} \right] \cdot |\beta\alpha\rangle^0$$

$$\boxed{|\alpha\beta\rangle' = |\alpha\beta\rangle^0 + \frac{J |\beta\alpha\rangle^0}{2\Delta}}$$

$$\cancel{|\alpha\beta\rangle' = |\alpha\beta\rangle^0 + \sum \left\langle \begin{matrix}\beta\alpha \\ \alpha\alpha \\ \beta\beta\end{matrix} \middle| \vec{I}_1 \cdot \vec{I}_2 \middle| \alpha \right.}$$

$|\cancel{\beta\alpha}$

$$|\beta\alpha\rangle' = |\beta\alpha\rangle^0 + J \sum \frac{{}^0\left\langle \begin{matrix}\alpha\alpha \\ \beta\beta \\ \alpha\beta\end{matrix} \middle| \vec{I}_1 \cdot \vec{I}_2 \middle| \beta\alpha \right\rangle^0}{E_* - E_{\beta\alpha}} |*\rangle$$

$$\langle \alpha\beta | I_{1+} I_{2-} | \beta\alpha \rangle = 1$$

$$\therefore\ |\beta\alpha\rangle' = |\beta\alpha\rangle^0 + J \frac{{}^0\langle \alpha\beta | I_{1+} I_{2-} | \beta\alpha \rangle^0}{E_{\alpha\beta} - E_{\beta\alpha}} |\alpha\beta\rangle^0$$

$$\boxed{|\beta\alpha\rangle' = |\beta\alpha\rangle^0 + \frac{J|\alpha\beta\rangle^0}{-2\Delta}}$$

$$|\alpha\alpha\rangle' = |\alpha\alpha\rangle^0$$

$$|\beta\beta\rangle' = |\beta\beta\rangle^0$$

$$E^{2} = {}^{0}\langle i^{0} | H_J | i^{0} \rangle^{1}$$

$$H_J = \left[I_{1z} I_{2z} + \frac{I_{1-} I_{2+} + I_{1+} I_{2-}}{2} \right] J$$

For $|\alpha\alpha\rangle^{1} = |\alpha\alpha\rangle^{0}$

$$E^{2}_{\alpha\alpha} = {}^{0}\langle \alpha\alpha | H_J | \alpha\alpha \rangle^{0} = \langle \alpha\alpha | I_{1z} I_{2z} J | \alpha\alpha \rangle$$

$$\boxed{E^{2}_{\alpha\alpha} = \frac{J}{4}}$$

$|\beta\beta\rangle^{1} = |\beta\beta\rangle$ $\quad E^{2}_{\beta\beta} = {}^{0}\langle \beta\beta | I_{1z} I_{2z} J | \beta\beta \rangle^{0} = \frac{J}{4}$

$$|\alpha\beta\rangle^{1} = |\alpha\beta\rangle^{0} + \frac{J |\beta\alpha\rangle^{0}}{2\Delta}$$

$$E^{2}_{\alpha\beta} = {}^{0}\langle \alpha\beta | H_J | \alpha\beta \rangle^{1}$$

$$= J\, {}^{0}\langle \alpha\beta | I_{1z} I_{2z} + \frac{I_{1+} I_{2-} + I_{1-} I_{2+}}{2} | \alpha\beta \rangle^{0}$$

$$+ J \langle \alpha\beta | \frac{+- + -+}{2} | \frac{J}{2\Delta} \beta\alpha \rangle^{0}$$

$$= J\, {}^{0}\langle \alpha\beta | I_{1z} I_{2z} | \alpha\beta \rangle^{0} + \frac{J^{2}}{4\Delta} \langle \alpha\beta | +- | \beta\alpha \rangle$$

$$E^{(2)}_{\alpha\beta} = \frac{-J}{4} + \frac{J^{2}}{4\Delta}$$

$$E^{(2)}_{\beta\alpha} = J\,{}^{0}\langle i|H_J|i\rangle'$$

$$\boxed{|\beta\alpha\rangle' = |\beta\alpha\rangle^{0} - \frac{J}{2\Delta}|\alpha\beta\rangle^{0}}$$

$$= J\langle\beta\alpha|\left[I_{1z}I_{2z} + \frac{+-+-+}{2}\right]|\beta\alpha^{0}\rangle$$

$$-J\,{}^{0}\langle\beta\alpha|[\ \ ]|\frac{J}{2\Delta}\alpha\beta\rangle^{0}$$

$$= J\,{}^{0}\langle\beta\alpha|I_{1z}I_{2z}|\beta\alpha\rangle^{0} - \frac{J^2}{4\Delta}\,{}^{0}\langle\beta\alpha|{}^{+}_{-}{}^{-}_{+}|\alpha\beta\rangle^{0}$$

$$\boxed{E^{(2)}_{\beta\alpha} = \frac{-J}{4} - \frac{J^2}{4\Delta}}$$

$$E^{(2)}_{\alpha\alpha} = E^{(2)}_{\beta\beta} = \frac{J}{4} \qquad \Delta = E_{\alpha\beta} - E_{\beta\alpha}$$

$$E^{(2)}_{\beta\alpha} = -\frac{J}{4} - \frac{J^2}{4\Delta}$$

$$E^{(2)}_{\alpha\beta} = \frac{-J}{4} + \frac{J^2}{4\Delta}$$

III-18g Magnetic equivalence: calculate the spectral frequencies arising from an A_2B system with shifts (ω_A) & (ω_B) & J-coupling (J). Demonstrate that the frequencies of the allowed transitions are independent of A-A J-coupling

~~AAB~~ $AA'B$

$$\boxed{\begin{aligned}\hat{H} &= -\Delta\omega_A F_{zA} - \Delta\omega_B I_{zB} + J_{AB}\,\bar{F}_A\cdot\bar{I}_B + J_{AA}\,\bar{I}_A\cdot\bar{I}_A \\ \bar{F}_A &= \bar{I}_{A_1} + \bar{I}_{A_2}\end{aligned}}$$

$\Delta\omega_A = \omega_A - \omega$ (carrier)

$\omega_{A_1} = \omega_{A_2}$

$\bar{I}_{A_1} = \bar{I}_{A_2}$

$$\therefore\ \hat{H} = -\Delta\omega_A(\bar{I}_{A_1} + \bar{I}_{A_2}) - \Delta\omega_B \bar{I}_{zB} + J_{AB}\,\bar{F}_A\cdot\bar{I}_B + J_{AA}\,\bar{I}_A\cdot\bar{I}_A$$

$$\hat{H} = -2\Delta\omega_A \bar{I}_A - \Delta\omega_B I_{zB} + J_{AB}(\bar{I}_{A_1} + \bar{I}_{A_2})\cdot\bar{I}_B + J_{AA}(\bar{I}_{A_1}\cdot\bar{I}_{A_2})$$

The $J_{AA}\,\bar{I}_A\cdot\bar{I}_A \Rightarrow J(I_{Ax}^2 + I_{Ay}^2 + I_{Az}^2) = J_{AA}\,\bar{I}^2$

$$J_{AA}\,\bar{I}_A\cdot\bar{I}_A = \frac{3}{4}\hbar^2\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}J = \frac{3}{4}\hbar^2\,\mathbb{1}\cdot J_{AA}$$

(No spin)

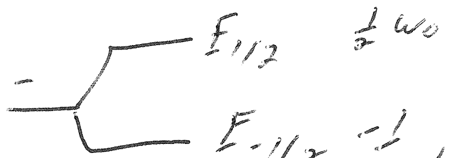
$+\frac{3}{4}\hbar^2 J_{AA}$ is an energy shift only & doesn't effect transition freqs!

$$H = -\bar{\mu}\cdot\bar{B} = -\gamma B_0 \bar{S}_z = -\omega_0 S_z$$

$$\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}1\\ 0\end{pmatrix} = \begin{pmatrix}1\\ 0\end{pmatrix} \text{ eg}$$

$H|\alpha\rangle =$

$H|\beta\rangle$



Lahr Freq $= \hbar\omega_0$

For $\frac{3}{4}\hbar^2 J_{AA}|\alpha\alpha\rangle = c|\alpha\alpha\rangle$ $|\alpha\alpha\rangle$ — — $|\alpha\beta\rangle$ — $|\beta\alpha\rangle$ — $|\beta\beta\rangle$

$\frac{3}{4}\hbar^2 J_{AA}|\alpha\beta\rangle = c|\alpha\beta\rangle$ ~~energy~~ levels don't change
& no observable transition

$\boxed{\text{Note all shift equally @ } \frac{3}{4}\hbar^2 J_{AA} \text{ however}}$

HAMILTONIAN NOW:

$\Delta w_A = |w_A| = (w_A - w)$

$$\boxed{\hat{H} = -2\Delta w_A F_{AZ} - \Delta w_B I_{BZ} + J_{AB}(F_A \cdot I_B)} + c \quad \text{ignore}$$

& 3 spin ∴ build on old

$$F_Z = \frac{1}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix} \otimes \begin{pmatrix}1&0\\0&1\end{pmatrix} + \frac{1}{2}\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}1&0\\0&-1\end{pmatrix} \qquad (I_{1ZA} + I_{2ZA}) = F_Z$$

$$F_Z = \frac{1}{2}\begin{pmatrix}1&0&0&0\\0&-1&0&0\\0&0&+1&0\\0&0&0&-1\end{pmatrix} + \frac{1}{2}\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix} = \begin{pmatrix}1&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&-1\end{pmatrix}$$

& now expand to 3-spin $|\alpha\alpha\alpha\rangle, |\alpha\alpha\beta\rangle \ldots |\beta\beta\beta\rangle$

To expand recall

2 spin $\begin{cases} I_{1Z} \otimes \begin{pmatrix}1&0\\0&1\end{pmatrix} \\ \begin{pmatrix}1&0\\0&1\end{pmatrix} \otimes I_{2Z} \end{cases}$

3 spin $\quad \begin{pmatrix}1&0\\0&1\end{pmatrix} \otimes \begin{pmatrix}1&0\\0&1\end{pmatrix} \otimes I_{3Z}$

$$F_{ZA} = \begin{pmatrix} 1&0&0&0\\ 0&0&0&0\\ 0&0&0&0\\ 0&0&0&-1 \end{pmatrix} \otimes \begin{pmatrix} 1&0\\ 0&1 \end{pmatrix} = \begin{pmatrix} \begin{matrix} 1&0&0&0\\ 0&0&0&0\\ 0&0&0&0\\ 0&0&0&-1 \end{matrix} & 0 \\ 0 & \begin{matrix} 1&0&0&0\\ 0&0&0&0\\ 0&0&0&0\\ 0&0&0&-1 \end{matrix} \end{pmatrix}$$

$$I_{BZ} = \begin{pmatrix} 1&0\\ 0&1 \end{pmatrix} \otimes \begin{pmatrix} 1&0\\ 0&1 \end{pmatrix} \begin{pmatrix} 1&0\\ 0&-1 \end{pmatrix} \frac{1}{2}$$

$$= \frac{1}{2} \begin{pmatrix} 1&0&0&0\\ 0&1&0&0\\ 0&0&1&0\\ 0&0&0&1 \end{pmatrix} \otimes \begin{pmatrix} 1&0\\ 0&-1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} \begin{matrix} 1&0&0&0\\ 0&1&0&0\\ 0&0&1&0\\ 0&0&0&1 \end{matrix} & 0 \\ 0 & \begin{matrix} -1&0&0&0\\ 0&-1&0&0\\ 0&0&-1&0\\ 0&0&0&-1 \end{matrix} \end{pmatrix}$$

$$F_{AZ} \cdot I_{BZ} = \frac{1}{2} \begin{pmatrix} \begin{matrix} 1&0&0&0\\ 0&0&0&0\\ 0&0&0&0\\ 0&0&0&-1 \end{matrix} & 0 \\ 0 & \begin{matrix} -1&&&0\\ &0&&\\ &&0&\\ 0&&&1 \end{matrix} \end{pmatrix}$$

---

recall $\vec{H} = -2w_A F_{ZA} - w_B I_{ZB} + J_{AB} \vec{F}_A \cdot \vec{I}_B$

*All diag components Thank full X

$$\begin{array}{c|cc} & \alpha & \beta \\ \hline \alpha & & \\ \beta & & \end{array} \quad \otimes \quad \begin{array}{c} \\ \alpha \\ \beta \end{array}\begin{array}{c} \begin{array}{cc} \alpha & \beta \end{array} \\ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{array}$$

$$\alpha\alpha \quad \beta\alpha \quad \alpha\beta \quad \beta\beta \quad \otimes \quad \begin{array}{c} \begin{array}{cc} \alpha & \beta \end{array} \\ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{array}$$

$\hat{H} =$	$-2\omega_A I_{zA}$	$-\omega_B I_{zB}$	$J_{AB} I_A \cdot I_B$
$\alpha\alpha\alpha$	$-\omega_a$	$-\frac{\omega_B}{2}$	$+J_{AB}/2$
$\beta\alpha\alpha$		$-\omega_B/2$	
$\alpha\beta\alpha$		$-\omega_B/2$	
$\beta\beta\alpha$	$+\omega_a$	$-\omega_B/2$	$-J_{AB}/2$
$\alpha\alpha\beta$	$-\omega_a$	$+\omega_B/2$	$-J_{AB}/2$
$\beta\alpha\beta$		$+\omega_B/2$	
$\alpha\beta\beta$		$+\omega_B/2$	
$\beta\beta\beta$	ω_A	$+\omega_B/2$	$+J_{AB}/2$

* Note $\frac{1}{2}$ terms come from $\hat{I}_z$; Diag matrix ∴ These are all E terms / EVs.

* $\mathrm{Det}(\hat{H} - \lambda \mathbb{1}) = 0$ ~~Though ...~~

$\lambda = eV$, $\hat{A} = \hat{H}$

$\lvert AA'B \rangle$ $\lvert \psi \rangle$	E
$\overline{\lvert \beta\beta\beta \rangle}$	$\omega_a + \frac{\omega_b}{2} + \frac{J}{2}$
$\overline{\lvert \beta\alpha\beta \rangle}$ $\overline{\lvert \alpha\beta\beta \rangle}$	$\omega_b / 2$
$\overline{\lvert \beta\beta\alpha \rangle}$	$\omega_A - \frac{\omega_b}{2} - \frac{J}{2}$
$\overline{\lvert \alpha\alpha\beta \rangle}$	$-\omega_A + \frac{\omega_b}{2} - \frac{J}{2}$
$\overline{\lvert \alpha\beta\alpha \rangle}$ $\overline{\lvert \beta\alpha\alpha \rangle}$	$-\frac{\omega_b}{2}$
$\overline{\lvert \alpha\alpha\alpha \rangle}$	$-\omega_a - \frac{\omega_b}{2} + \frac{J}{2}$

Look for F^+ transitions

$\lvert \alpha\alpha\alpha \rangle \rightarrow \lvert \alpha\beta\alpha \rangle$ & $\lvert \beta\alpha\alpha \rangle$ $(\omega_a + J/2)$

$\lvert \alpha\alpha\alpha \rangle \rightarrow \lvert \alpha\alpha\beta \rangle$ (ω_b)

$\lvert \alpha\beta\alpha \rangle$ & $\lvert \beta\alpha\alpha \rangle \rightarrow \lvert \beta\beta\alpha \rangle$ $(\omega_a - J/2)$

$\alpha\alpha\alpha \rightarrow \alpha\alpha\beta$ $\quad W_B - J$

$\alpha\alpha\alpha \rightarrow \alpha\beta\alpha$ $\quad W_a \mp J/2$

$\alpha\alpha\alpha \rightarrow \beta\alpha\alpha$

$\alpha\beta\alpha \rightarrow \beta\beta\alpha$ $\quad W_a - J/2$

$\beta\alpha\alpha \rightarrow \beta\beta\alpha$

$\alpha\alpha\beta \rightarrow \alpha\beta\beta$ $\quad W_a + J/2$

$\alpha\alpha\beta \rightarrow \beta\alpha\beta$

$\beta\beta\alpha \rightarrow \beta\beta\beta$ $\quad W_B + J$

$\beta\alpha\beta \rightarrow \beta\beta\beta$ $\quad W_a + J/2$

$\alpha\beta\beta \rightarrow \beta\beta\beta$

$\alpha\beta\alpha \rightarrow \alpha\beta\beta$ $\quad W_B$

$\beta\alpha\alpha \rightarrow \beta\alpha\beta$ $\quad W_B$

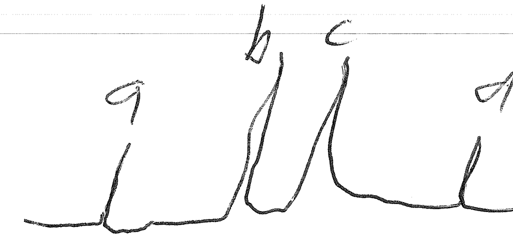
IV-19) 60 MHz ^1H spectrometer of an AB system gives the following peaks in Hz:

$423 = \nu_a$

$418.5 = \nu_b$

$416 = \nu_c$

$411.5 = \nu_d$



AB - system

1) δ_a δ_b & $J = ?$

$$\boxed{\begin{array}{l} \Sigma = \dfrac{\nu_a + \nu_d}{2} = \dfrac{\nu_b + \nu_c}{2} \\ J = \nu_b - \nu_a = \nu_d - \nu_c \\ |\Delta| = \sqrt{(\nu_a - \nu_d)(\nu_b - \nu_c)} \end{array}}$$

$J = 416.0 - 411.5 = 4.5\ Hz$

$\Sigma = \dfrac{423 + 411.5}{2} = \dfrac{834.5}{2}$

$\Sigma = 417.25$

$\Delta = \sqrt{(423 - 411.5)(418.5 - 416)}$

$= \sqrt{11.5 \times 2.5} = 5.36$

$\delta_A = \dfrac{\Sigma + \frac{\Delta}{2}}{\text{carmel}}$ $\quad$ $\delta_B = \dfrac{\Sigma - \frac{\Delta}{2}}{\text{carmel}}$

$\boxed{\delta = \dfrac{417 + 2.7}{60} = 7.0\ ppm\ @\ 60\,MHz}$ $\quad$ $\boxed{\delta_B = \dfrac{417 - 2.7}{60} = 6.9\ ppm\ @\ 60\,MHz}$

$= \cancel{1.4\ ppm\ @\ 300}$ $\quad$ $= \cancel{1.38\ ppm\ @\ 300\,MHz}$

position of 4 pks if expt is acquired @ 300

$\delta_a = 7.0 \times 300 \pm \frac{J}{2}$ → 2102.2 ν_a, 2098 ν_b $\quad \frac{J}{2} = 2.2\ Hz$

$\delta_B = 6.9 \times 300 \pm \frac{J}{2}$ → 2072 ν_c, 2068 ν_D

J - Field independent

III-20) Construct the Hamiltonian matrix for an ABX system

- can this mat be diagonalized?

$$\boxed{\hat{H} = -\sum_k w_k I_{zk} + \sum_{i<k}\sum_k J_{ik}\,\bar{I}_i \cdot \bar{I}_k}$$

$k = a, b, X$

$$\boxed{\begin{aligned}\hat{H} &= -w_A I_{zA} - w_B I_{zB} - w_X I_{zX} \\ &+ J_{AB}\,\bar{I}_A \cdot \bar{I}_B + J_{AX}\,\bar{I}_A \cdot \bar{I}_X + J_{BX}\,\bar{I}_B \cdot \bar{I}_X\end{aligned}}$$

3 spin need to expand on basis t

$\boxed{\text{F-terms}}$

$$A = \frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$

$$B = \frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$

$$X = \frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

Note 1st order perturbative approx needed here.

$w_A - w_X \gg J$

$w_B - w_X \gg J$

truncate to Z

$w_a - w_B \sim J$

can't use here

$$\boxed{\begin{aligned}\hat{H} &= -w_A I_{zA} - w_B I_{zB} - w_X I_{zX} \\ &+ J_{AX}\,\bar{I}_{zA} \cdot \bar{I}_{zX} + J_{BX}\,\bar{I}_{zB} \cdot \bar{I}_{zX} \\ &+ J_{AB}\left(\bar{I}_A \cdot \bar{I}_B\right)\end{aligned}}$$

$$F_{AZ} = \frac{1}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}1&0\\0&1\end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&1&\end{pmatrix}$$

$$F_{AZ} = \frac{1}{2}\left(\begin{array}{cccc|cccc}1&0&0&0&0&0&0&0\\0&-1&0&0&0&0&0&0\\0&0&1&0&0&0&0&0\\0&0&0&-1&0&0&0&0\\ \hline 0&0&0&0&1&0&0&0\\0&0&0&0&0&-1&0&0\\0&0&0&0&0&0&1&0\\0&0&0&0&0&0&0&-1\end{array}\right)$$

$$F_{BZ} = \frac{1}{2}\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}1&0\\0&1\end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}1&0&0&0\\0&-1&0&0\\0&0&1&0\\0&0&0&-1\end{pmatrix} = \left(\begin{array}{cccc|cccc}1&0&0&0&0&0&0&0\\0&-1&0&0&0&0&0&0\\0&0&-1&0&0&0&0&0\\0&0&0&-1&0&0&0&0\\ \hline 0&0&0&0&1&0&0&0\\0&0&0&0&0&1&0&0\\0&0&0&0&0&0&-1&0\\0&0&0&0&0&0&0&-1\end{array}\right)\frac{1}{2}$$

$$\cancel{F_{XZ}} = \frac{1}{2}\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}1&0\\0&-1\end{pmatrix}$$

$$F_{XZ} = \frac{1}{2}\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix} = \frac{1}{2}\left(\begin{array}{cccc|cccc}1&0&0&0&0&0&0&0\\0&1&0&0&0&0&0&0\\0&0&1&0&0&0&0&0\\0&0&0&1&0&0&0&0\\ \hline 0&0&0&0&-1&0&0&0\\0&0&0&0&0&-1&0&0\\0&0&0&0&0&0&-1&0\\0&0&0&0&0&0&0&-1\end{array}\right)$$

$\cancel{F_A}$ $\boxed{\text{Need } F_{A+}\ F_{B+}\ F_{A-}\ F_{B-} \text{ terms too}}$

$$F_{A+} = \begin{pmatrix}0&1\\0&0\end{pmatrix}\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}1&0\\0&1\end{pmatrix} = \begin{pmatrix}0&1\\0&0\end{pmatrix}\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}$$

$$F_{A+} = \left(\begin{array}{cccc|cccc}0&1&0&0&0&0&0&0\\0&0&0&0&0&0&0&0\\0&0&0&1&0&0&0&0\\0&0&0&0&0&0&0&0\\ \hline 0&0&0&0&0&1&0&0\\0&0&0&0&0&0&0&0\\0&0&0&0&0&0&0&1\\0&0&0&0&0&0&0&0\end{array}\right)$$

$$F_{B+} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$F_{B+} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{pmatrix} = \left(\begin{array}{cccc|cccc} 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array}\right)$$

$$F_{A-} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \left(\begin{array}{cccc|cccc} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \end{array}\right)$$

$$F_{B-} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$= \begin{matrix} 1 & 0 \\ 0 & 1 \end{matrix} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = \left(\begin{array}{cccc|cccc} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{array}\right)$$

$$\boxed{I_A \cdot I_B = I_{zA} I_{zB} + \frac{I_{A+} I_{B-} + I_{A-} I_{B+}}{2}}$$

$$F_{Az} F_{Bz} = \frac{1}{4}\left[\, 1 \;\; -1 \;\; -1 \;\; +1 \;\;\; 1 \;\; -1 \;\; -1 \;\; 1 \,\right] \text{ diag}$$

$$F_{Az} F_{Xz} = \frac{1}{4}\left[\, 1 \;\; -1 \;\; 1 \;\; -1 \;\;\; -1 \;\; 1 \;\; -1 \;\; 1 \,\right] \text{ diag}$$

$$F_{Bz} F_{Xz} = \frac{1}{4}\left[\, 1 \;\; 1 \;\; -1 \;\; -1 \;\;\; -1 \;\; -1 \;\; 1 \;\; 1 \,\right] \text{ diag}$$

$$F_{A+} \cdot F_{B-} = \left[\begin{array}{cccc|cccc}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{array}\right]$$

sep row sec col

LOOK DOWN COLUMNS OF 2ND TERM. IF ZEROS THEN COLUMN IS ZERO

$$F_{A-} F_{B+} = \left[\begin{array}{cccc|cccc}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{array}\right]$$

$$\boxed{\hat{H} = -\omega_A I_{zA} - \omega_B I_{zB} - \omega_X I_{zX} + J_{AX} I_{zA} I_{zB} + J_{BX} I_{zB} I_{zX} + J_{AB}(\bar{I}_A \cdot \bar{F}_B)}$$

Diagonal

			$F_{Az}F_{Bz}$	$F_{Az}F_{Xz}$	$F_{Az}F_{Xz}$	$J_{AB}I_AI_B$
$-\omega_A/2$	$-\omega_B/2$	$-\omega_C/2$	$+J_{AB}/4$	$+J_{AX}/4$	$+J_{BX}/4$	
$\omega_A/2$	$-\omega_B/2$	$-\omega_C/2$	$-J_{AB}/4$	$-J_{AX}/4$	$+J_{BX}/4$	$+J_{AB}/2$
$-\omega_A/2$	$+\omega_B/2$	$-\omega_C/2$	$-J_{AB}/4$	$+J_{AX}/4$	$-J_{BX}/4$	$+J_{AB}/2$
$\omega_A/2$	$+\omega_B/2$	$-\omega_C/2$	$+J_{AB}/4$	$-J_{AX}/4$	$-J_{BX}/4$	
$-\omega_A/2$	$-\omega_B/2$	$+\omega_C/2$	$+J_{AB}/4$	$-J_{AX}/4$	$-J_{BX}/4$	
$\omega_A/2$	$-\omega_B/2$	$+\omega_C/2$	$-J_{AB}/4$	$+J_{AX}/4$	$-J_{BX}/4$	$+J_{AB}/2$
$-\omega_A/2$	$+\omega_B/2$	$+\omega_C/2$	$-J_{AB}/4$	$-J_{AX}/4$	$+J_{BX}/4$	$+J_{AB}/2$
$\omega_A/2$	$+\omega_B/2$	$+\omega_C/2$	$+J_{AB}/4$	$+J_{AX}/4$	$+J_{BX}/4$	

See Last page for off Diag elements here. ie $J_{AB}\bar{F}_A \cdot F_B$ part

$$J_{AB}\left(\frac{F_{A+}F_{B-} + F_{A-}F_{B+}}{2}\right) =$$

$$\frac{1}{2}\left(\begin{array}{cccc|cccc}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\hline
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{array}\right) \cdot J_{AB}$$

∗ in Matrix above there are two Quadrants w/ off diag ~~TERMS~~ TERMS

- we could Diagonilize by changing Basis set